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Third International Workshop on
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and Air Purification
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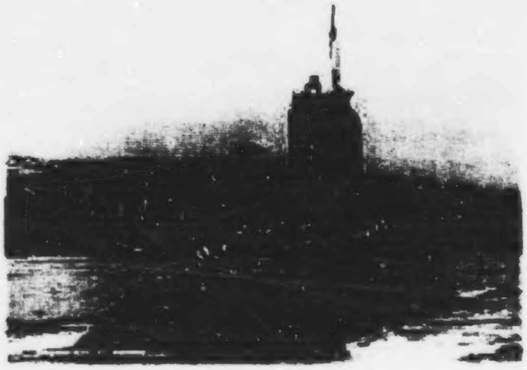
Part 1



Partie 1

SPASM 2000 - Actes

Troisième Conférence
sur la surveillance et la purification
de l'air dans les sous-marins
11-13 octobre 2000 à
Toronto, Canada

Canada

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Forty Years of Air Monitoring on American Nuclear Submarines

Third Submarine Atmosphere Purification and Monitoring Conference
Toronto Canada, October 11, 2000

by Dr. Jeffrey R. Wyatt
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Good morning. It's a pleasure to be here and present the keynote address. I would like to thank the organizers for asking me to speak and providing this site. I have always enjoyed my visits to Canada and was pleased when I learned that the Third SAMAP was being held here. When I reflected on which aspect of submarine life support would be the best topic for this talk, I selected the history of atmosphere monitoring. Principally due to its dependence on electronics, the technology of atmospheric monitoring has changed more than that of the other equipment needed for life support. And it presents a more interesting, at least to me, subject to cover.

Submariners have always needed atmosphere monitoring equipment. Of course in the past on diesel submarines there was little that could be done to refurbish the atmosphere except for short term using chemical scrubbing and oxygen candles or tanks. The principal method of atmosphere control was surface ventilation so the requirements of the atmosphere monitoring were minimal. A former submariner remarked to me that you could always tell when the oxygen level was getting low because it became difficult to light your cigarettes. All of this changed when the USS NAUTILUS went to sea in 1954. As Admiral Stuart said in 1955, "With the advent of the nuclear-powered submarine, the problem of maintaining habitability of the atmosphere has arisen.".[1] This certainly is a prime example of a disruptive technology for the Navy. Suddenly a submarine could remain submerged for indefinite periods of time. In fact the Nautilus transited under the polar ice cap in 1958. Interestingly in preparation for this voyage the emergency air breathing system was installed which is now used on all of our submarines.

Additionally the availability of large amounts of power also resulted in an increased need for heat removal hence air conditioning, which required refrigerants. Early air conditioning systems often leaked refrigerants, which would build up in the atmosphere. Although the refrigerants were non-toxic, they would decompose in the burner to produce acid gases, which are both toxic and corrosive. The refrigerants would also decompose in lighted cigarettes, which gave an unpleasant taste so I have been told. Although nuclear submarines could stay submerged indefinitely, they would often surface or snorkel as a means of atmosphere purification. It was seldom necessary to remain submerged for extended periods. This requirement changed with the ballistic missile submarine developed in the early 1960's. Here long term submerged operation was the rule, which placed an increased emphasis on atmosphere control.

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[1] R. L. Stuart, Rear Admiral, Assistant Chief of the Bureau of Ships, 1955

During the 1960's one of the most troublesome areas of atmosphere control was the atmosphere monitor. The atmosphere monitors which had no special name went through six generations: the Mark I to Mark VI. The atmosphere monitor was always on the top ten list of systems needing critical attention and sometimes the top system. An example of the type of information I found in my historical files is the following letter written in 1962 which I quote:

> POLLACK will have a MK IV Atmosphere Analyzer installed. This equipment has been received at New York Shipbuilding Corporation and will be installed in an immediate future. I am concerned with apparent inadequacies and unreliability of this equipment so vital to the proper atmosphere control of a submerged submarine.[2]

The chronology of the atmosphere analyzers is shown on the next slide. In general terms how the analyzers worked as follows. The Mark I to Mark IV and Mark VI used an oxygen meter based paramagnitism, a hydrogen meter based on thermo-conductivity and infrared adsorption for everything else. The CAMS use infrared for carbon monoxide and mass spectrometry for everything else.

Photographs of the analyzers are shown on the following slides. We don't have any photos of the Mark I. It was a prototype that was installed on the USS NAUTILUS but never operated. The Mark II is shown on the next slide. Interestingly the Mark II had an infrared sensor for hydrocarbons but not for refrigerants. The full scale reading for the analog meter for hydrocarbons was 5 mm of mercury or about 6,[illegible]00 ppm. The Mark III shown on the next slide was designed to detect refrigerants and [illegible] hydrocarbons. In order increase the sensitivity, the infrared cells were pressurized to 100 psi. The pressurized cells and infrared systems were not reliable. In fact the instrument had so many failures that the infrared portion was turned off between readings in order to attempt to improve its time between failures. To improve both the reliability and sensitivity of the infrared system, the Mark IV, shown on the next slide, used infrared cell cells that were unpressurized but about four feet (120 cm) long. For this reason the Mark IV was much taller than the previous systems. Although better than the Mark III, the Mark IV was still failure prone.

All of these systems used infrared analyzers that were not particularly reliable and lacked sensitivity to detect small refrigerant leaks. Unlike most situations, the submarine analyzer must operate within the environment that it is analyzing. This led to the problem that the refrigerants that leaked into the atmosphere were decomposed by the heated infrared source of the analyzer, which led to degradation and eventual failure of the source. Since the analyzer provided poor readings, it was not believed and small leaks of refrigerant were not noticed--an example of a typical viscous circle. A solution was to develop the Mark V, shown on the next slide, which used an automated gas chromatograph to analyze all of the gases. Perhaps today one could build such as system well enough to meet the challenge of submarine air analysis. But not then, the Mark V was a real disaster. Finally, a new atmosphere analyzer the Mark VI, shown on the next slide, was built based upon Mark IV technology. It was built by a different, smaller, low bid vendor, and was less reliable than the Mark IV. Essentially things had gone from bad to worse. Which analyzer should the Navy buy for its more than 100 nuclear submarines?

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[2] H. E. Lyon, Prospective Commander USS POLLACK SSN 603, letter to the Chief of the Bureau of Ships, 17 July 1962

Finally at this point Dr. Fred Saalfeld of the Naval Research Laboratory was able to convince the Navy to evaluate an analyzer based on the perceived exotic technique of mass spectrometry. A small air analyzer was available which had been built by Perkin Elmer Aerospace Division[3] as a prototype for NASA Skylab program. It was mounted in the torpedo room of the USS HAMMERHEAD and the crew instructed to record and compare its readings with those from the Mark IV analyzer onboard. Two days at sea and the Mark IV failed. The test analyzer worked fine the entire trip which lasted 45 days. Because of this successful test, two prototype submarine atmosphere analyzers were built and installed on the submarines USS HAWKBILL and USS PINTADO. The units gave such excellent performance that the crew requested that they remain on board after the test was over – always a good sign. During this time Bob Olfky, a member of Dr. Saalfeld's group coined the acronym CAMS for Central Atmosphere Monitoring System. Bob would go anywhere, anytime to visit a submarine and frequently did. Here is a photo of the CAMS-I prototype with Bob Olfky. A production version of the CAMS was built and tested to all the rigorous acoustic, EMI, shock and vibration requirements for submarine equipment. None of the previous systems could have passed these tests. Here is a photo of the production CAMS-I. Incidentally in 1998 and 1999 the USS HAWKBILL relying on its CAMS-I analyzer which has remained virtually unchanged in the last 25 years, participated in a scientific polar ice cap experiment. These experiments, called SCIEX, have a nice site on the web.

Finally twenty years after the Nautilus, the Navy had a reliable atmosphere analyzer for submarines. During the next five years sufficient CAMS were produced to equip all United States nuclear submarines. The CAMS uses mass spectrometry to measure all of the gases except carbon monoxide which is measured by an infrared analyzer. The infrared analyzer uses a special method of measurement developed by the Andros Corporation that is only applicable to carbon monoxide and it has proven to be very reliable. One clever innovation was to use a heating element from an automobile cigarette lighter as an infrared source. There have been few problems with this source. Of course the refrigerant levels that it is exposed to are much lower due to performance of the CAMS-I. When the submarine crew observed the CAMS displaying an increasing level of refrigerant, they became confident that there really was leak and would find and correct it

During the 1960's because the regular atmosphere analyzer could not measure hydrocarbons, a special instrument was developed for this purpose. It was a small gas chromatograph with a flame ionization detector and it operated like laboratory instruments used for the same purpose. A photograph of it is shown on the next slide. When it worked, it gave good data. Unfortunately it often had problems and was difficult for the sailors to maintain. One sixteenth inch tubing fittings is one example of the items routinely used in the laboratory but difficult for sailors. Don't get me wrong I have the greatest respect for the sailors I met and worked with on our submarines. The total hydrocarbon analyzer (THA) developed a bad reputation and eventually was removed from submarines due to its unreliability. In the 1980's the THA was replaced with a much simpler system to measure hydrocarbons based on photoionization. It is called the Trace Gas Analyzer or TGA and is shown on the next slide.

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[3] Now part of the Orbital Sciences Corporation.

As the first production CAMS were being installed, Dr Saalfeld had the vision to realize that a second-generation CAMS analyzer was needed. I still remember in 1975 Dr. Saalfeld discussing with me what performance specifications should the CAMS-II have. The principal reason for the second-generation analyzer was the inability of the CAMS-I to detect trace hydrocarbons and its hardwired method of detection making it difficult to change which species it detects. Convincing the Navy of the need for a CAMS-II was not easy. After all CAMS-I's were not even yet installed on all of our submarines. Unlike the previous analyzers the CAMS-I was reliable and not a problem piece of equipment. Fortunately Dr Saalfeld prevailed and the CAMS-II became a reality and is now used on all of our Trident and newer attack submarines.

Unlike the CAMS-I development, which was a crash program as you can infer from the next slide, the CAMS-II development took much longer. The time from the development contract to the first installation of the first production CAMS-II was twelve years and shown on the next slide. It is representative of why it can take so long to build military equipment. I want to spend some time discussing this chronology. The principal reason for this length of time was the extensive testing required to prove that the CAMS-II would be as reliable as the CAMS-I. Additionally there was no clamor from the fleet for an improved CAMS-I. In order to reduce installation costs, the CAMS-II was designed to be identical in form and fit to the CAMS-I as you can see on the following slide showing the CAMS-II and CAMS-I side by side during testing at NRL.

During the CAMS-II development my principal concern was that the CAMS-II would be significantly less reliable than the CAMS-I which would prevent it from being accepted by the Navy. I had my own doubts. No one had any experience operating a medium performance mass spectrometer continuously for two years. Would the system maintain its performance and not degrade? Two years was the figure of merit as it is the typical life the filament in the CAMS-I. In addition, the more complicated electronics were also a potential failure source. Fortunately my concerns were unnecessary. For example the following viewgraph shows two years' data from the CAMS-II prototype during operational testing. Another concern all of us in the program had was would the CAMS-II survive the shock and vibration testing or for that matter even retesting the system. I certainly had my fingers crossed each of the six times the hammer slammed into the base of the shock test machine. Fortunately the only effect was a glitch in the set of readings being taken during the impact--a real tribute to the engineers that designed the CAMS-II. In fact it gave correct readings all during the vibration test as well.

The performance of the CAMS-I and CAMS-II is similar for hydrogen, nitrogen, oxygen, and carbon dioxide. Note both systems also measure water vapor, which is necessary in order to calculate accurately the partial pressure of the above gases. The accuracy of these systems is remarkable and is on the order of one percent. Refrigerant levels can be measured to one ppm. The systems are so good that they do not need to be recalibrated after leaving the factory. A verification gas is used to confirm operation aboard ship. In addition reliably obtaining test gases to this accuracy is not trivial. We have had mixed results in obtaining good test gases in the past and trust our CAMS units more than the test gases. Even the CAMS manufacturer has received certified test gases that were incorrect.

As I mentioned earlier, one advantage of the CAMS-II over the CAMS-I is ease of reprogramming. Like the rest of the world, the Navy is switching from CFC refrigerants to HFC refrigerants. This requires modifying the atmosphere analyzers to detect the HFC refrigerants. The CAMS-I required modifying the analyzer during overhaul. This can be explained by understanding how the CAMS-I works. Here is a drawing from the CAMS-I manual. New ion collectors had to be added. A drawing showing the actual ion flights paths in the CAMS-I is shown on the next slide. With the CAMS-II a minor change in the software was all that was necessary. A depiction of the CAMS-II mass spectrometer is shown on the next slide. Here the magnetic field is varied to select the mass of interest. We specified that the CAMS-II software be table driven to make this type of software change straightforward.

In addition to the submarine atmosphere analyzers, near real time analyses have been performed on board using laboratory instrumentation operated by NRL scientists for many years. In the 1956 a habitability cruise was conducted in which a mass spectrometer, infrared analyzer, gas chromatograph and particle analyzers were used on board the NAUTILUS. The results of this cruise showed the high levels of hydrocarbons that were present and resulted in the ban on painting on board. It was shown that a catalytic burner was needed. The next slide shows some 1959 data from an NRL report. For anyone who has done submarine air sampling the characteristic signature of the hydrocarbons is unmistakable. Note the chromatogram reads from right to left. It is also interesting to note the comparison to paint thinner – not a bad match. Let's flash forward thirty-five years on the next slide. Here is some data I acquired operating a small portable gas chromatograph on a submarine. The data shows hydrocarbon levels before and after the burner.

Now that we have the luxury of hindsight, we may ask why the Navy did not build a CAMS-I in 1960. The simple answer is we couldn't. The CAMS-I requires very sensitive solid state electrometers capable of measuring currents as low as 10^{-14} amperes. These just were not available in 1960. In fact many the solid-state electronics used in CAMS-I were not available in 1960. The atmosphere analyzers have always been limited by the available technology. The enabling technology that made the CAMS-II possible is the microprocessor. Until the mid 1970's microprocessors were only fiction. Originally Dr. Saalfeld and I envisioned that the CAMS-II would be controlled by minicomputer. In fact this would have been difficult due to space limitations. We wanted the CAMS-II to be identical in size to the CAMS-I so that installation costs would be minimal. By the time the CAMS-II was being designed mil-spec microprocessors were available.

After reflecting on past, I would like to use this forum to provide some positive lessons learned and reflect upon the future. Much of the success of the CAMS program is due to the skills and dedication of many people both in the Navy and at Orbital Sciences Corp, formerly Perkin Elmer Aerospace Division, the manufacturer of the

CAMS systems. Also I believe it was important that some of those people stayed with the program for many years providing continuity to the program and a pride in ownership. Many of the people "rode" submarines and obtained a better appreciation of what was needed and what was not needed by the fleet – know your customer. We always arranged for new people both government and commercial to visit a submarine and talk to the CAMS operators. In the CAMS program and other programs that I have worked on we always established a relationship of trust with industry and shared problems as they occurred. When you are working on a system that will be used for a long time it's important to do it right the first time even if it takes longer. If you goof, you or someone else will have to live with your sins for a long time. After all, we are still using CAMS-I 's designed more than 25 years ago.

A time to pause can be good. Often real world systems that are committed to schedules -- including ourselves -- are caught on a treadmill. Sometimes one needs to standdown and assess how one is doing and make necessary changes. The most prominent example of this is the space shuttle program which by the mid 1980's needed to make a lot fixes. Unfortunately it took a disaster to force NASA to reassess the program. The two plus years of CAMS-II at sea testing and the time required to issue a production contract gave the program in effect a time to pause. Some of the changes that occurred during this time are shown on the next slide

Before closing, I would be remiss without acknowledging the many other people who contributed to the CAMS program. In particular I owe a debt to Dr. Fred Saalfeld whom I already mentioned who taught me about vision, Tom Daley, who has been involved with submarine life support longer than I have and taught me to think like an engineer, and Dr. James Decorpo who taught me to think like a project manager and view technology from a Navy perspective.

Categorisation of Substances found in Submarine Atmospheres

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Abstract

A multitude of substances have been detected in submarine atmospheres in the Royal Navy's experience over many years of submerged, closed-boat conditions. Some of these have greater potential to cause harm than others - likewise some are more amenable to detection and recording than others.

For some time the priority for toxicology assessment has been set by the perceived health risk, and the air monitoring capability required was strongly influenced by the state-of-the-art for instrumentation. Inconsistencies between the two requirements prompted a re-appraisal.

A new system of categorisation was devised which is risk-based. It is straightforward, provides a unified and coherent scheme to rank any substance according to the relative threat that it poses within the submarine, and indicates what monitoring methodology would be appropriate.

This paper describes the system of categorisation, its evolution and the rationale behind it.

Introduction

The diversity of chemical substances that have been found in submarine atmospheres is very wide. Some of them are harmless; some are vital; some are more dangerous than others. Some are there all the time, some appear very rarely, and others only occur in abnormal conditions.

With these extremely complex permutations of properties it is not easy to decide which substances deserve what level of priority treatment. A list in order of toxicity might at first sight appear to meet the needs of health protection, but would not be realistic if it didn't reflect the likelihood of the substance being there in appreciable quantities. Likewise, a list of substances developed according to which instrumentation was appropriate to each substance might not take into account their relative health significance.

Because resources are never unlimited, those responsible for submarine air purification have from time to time to take decisions on which development, or which equipment is to be given priority or deferred. If there is more than one way of classifying substances it doesn't help in taking these decisions. There is clearly a need to obtain an appreciation of the relative significance of substances found in the boat's atmospheres.

Background

The Royal Navy has been operating submarines for nearly a century, and nuclear submarines for about a third of that time. A lot of experience has been built up with the nuclear boats, which can stay submerged for long periods with a totally closed atmosphere, and a considerable range of substances have been detected at one time or another. Over the last 30 years the availability and sophistication of air monitoring instrumentation has advanced considerably, the understanding of how contaminants interact with each other in the atmosphere has grown, and the body of toxicological information has also developed. Each major step requires a re-appraisal of how the current policy is being implemented.

Previous Systems

Previous schemes for classifying substances had resolved themselves into two groups:

a) by toxicity and health risk
b) by monitoring method.

Both these methods met their sponsors' needs and coexisted in parallel, but separately.

When it became necessary to replace the submarines' continuous central air monitoring system (CAMS) we had to ask: "what *are* the substances that have to be monitored all the time, with the results available to ship's staff in real time?" Thinking about the list exposed the disparity of approaches between the two methods. The boundaries lay in different places, having been created for different purposes. This mis-match was felt to be confusing and thus a cause for concern and a solution was sought, breaking down the lists on a rational basis that was manageable, practical and able to command general support.

The Solution

The key lay in reviewing the "Threat" which each substance posed for the submarine and its crew, a concept which tied in with the risk-based safety management systems that it is now MoD's policy to introduce.

The process is shown in Diagram 1. Having defined five different levels of threat, the next stage identifies those with three very general groups by their need for monitoring: (i) needed in real-time on board; (ii) needed but not in real-time; and (iii) not needed at all. These are however too general to be an aid to decision-making. Below that a further level of subdivision was proposed which created five groups; these five, which the diagram clearly shows deriving from the threat groups, form the basis of the categorisation scheme now in use.

Defining the extremes of the scale proved to be the most straightforward part of the task. It was more contentious in the middle of the scale, where there were two potentially difficult areas to highlight where significant distinctions needed to be drawn:

a) between 'potential' threat substances and 'remote' threats, and
b) for 'remote' threat substances between those warranting routine retrospective monitoring, and the remainder not routinely monitored.

In practice, these nice distinctions have not proved to be as troublesome as at first it seemed they might be.

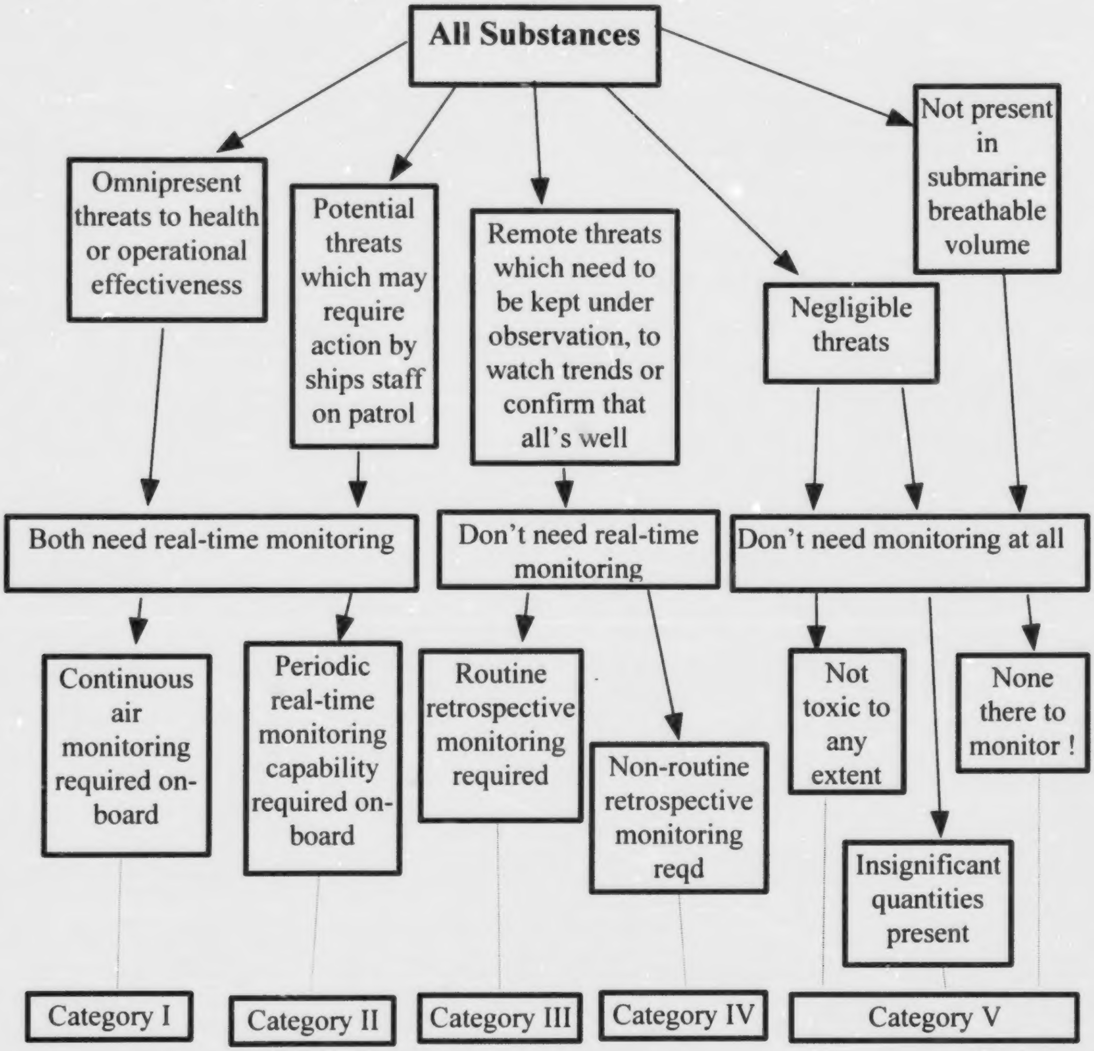
All Substances
Omnipresent threats to health or operational effectiveness
Potential threats which may require action by ships staff on patrol
Remote threats which need to be kept under observation, to watch trends or confirm that all's well
Negligible threats
Not present in submarine breathable volume
Both need real-time monitoring
Don't need real-time monitoring
Don't need monitoring at all
Continuous air monitoring required on-board
Periodic real-time monitoring capability required on-board
Routine retrospective monitoring required
Non-routine retrospective monitoring reqd
Not toxic to any extent
Insignificant quantities present
None there to monitor !
Category I
Category II
Category III
Category IV
Category V

DIAGRAM 1

Categorisation of substances by both hazard and monitoring requirements

Definitions of Categories

Our five Categories are taken from the output end, that is the bottom of the diagram: they are defined by qualitative descriptions, which are sufficiently detailed to convey what each means and the differences between them.

Category I The top priority list of life gases and major contaminants, warranting continuous monitoring on board.
Hazard level: *Omnipresent*
Monitoring requirement: *Continuous, real-time*

> Category II Substances which can in abnormal conditions (fire, machinery breakdown etc.) be a hazard during the course of a patrol; and on which ships staff need information *at the time* to contain the risk and make decisions on continued operation. Such substances must be measurable by ships staff at sea on an occasional basis either using portable or consumable instrumentation.
> Hazard level: *Potential*
> Monitoring requirement: *Periodic, Real-time*
>
> Category III Substances that are unlikely ever to pose an immediate threat to submariners' health or operational efficiency during a patrol, but which crop up with sufficient frequency and in significant quantities that long term health effects cannot be regarded as negligible. This would indicate to a responsible employer/ ship-owner that a *regular* account should be kept of these substances: both how often they occurred and in what concentrations. This justifies placing the duty on ships staff to carry out repeated sampling at defined intervals.
> Hazard level: *Remote, but still significant*
> Monitoring requirement: *Routine retrospective*
>
> Category IV Substances that no-one would seriously consider a hazard to either submarine or crew, but which do crop up and whose presence might conceivably tell the design and operating authorities something about the vessel that they ought to be aware of. It is sufficient to monitor for these substances occasionally only, and acceptable if special equipment has to be used for such occasional monitoring, which calls for skills beyond ships staff normal capabilities.
> Hazard level: *Remote, but not negligible*
> Monitoring requirement: *Non-routine retrospective, or special trials*
>
> Category V A repository for substances that have been assessed and - for a variety of reasons - written off as potential threats, therefore requiring no monitoring at all. It is considered wise to keep these as a list rather than simply strike them off, and prudent to review the list occasionally: just in case.
> Hazard level: *Negligible*
> Monitoring requirement: *Not monitored.*

What lies behind the distinction between Categories III and IV, i.e. between routine retrospective and non-routine? By definition, substances in neither category represent any immediate risk to health. The dividing line rests on an assessment of relative risk:

> Category III includes substances with *some health significance which have a reasonable likelihood of being present around or just under the threshold of health and safety interest i.e.* $\leq {}^{1}/_{10}$ *CES (continuous exposure standard),*
>
> whereas Category IV contains substances which aren't likely to qualify, either on grounds of *very low concentrations, very low probabilities or very low toxicities*, but which in turn *aren't so minuscule a risk as to be disqualified* from monitoring at all.

How it was done

Thus far all this discussion has been hypothetical: the test comes in assigning substances to categories. How would this be done?

The process was essentially based on consensus of a team of suitably qualified and experienced people, combining the disciplines of submarine medicine, toxicology, health and occupational hygiene, submarine air purification, material toxicity assessment, air monitoring instrumentation, submarine engineering, and ship safety management.

The starting point was the complete list of substances detected in submarine atmospheres over the years. Each was scrutinised for the threat it posed, and then assigned to a category. For an appreciable proportion there was no controversy; and the substance was categorised 'by inspection'. After all, who is going to argue with putting oxygen into Category I?

Which illustrates one clear lesson learnt: that it was easier to categorise the ends of the scale than it was the middle. The issues were more clear-cut and there was less scope for individual judgement. But many substances were nowhere as straightforward and a more structured approach was needed.

Where it was invoked, this took place in three stages:

> a) Historical record
> When had it last been detected? At what concentrations? What were typical levels? What had been the maximum observed? How frequently had it been detected?
>
> b) Risk analysis
> What are the possible sources of the substance onboard? How large a quantity? What are the mechanisms by which it might be released? And at what rate? What removal mechanisms are there on board? How rapidly could they remove it? Would it be distributed evenly through the boat? How might it be spread from its source? If it occurs, will ship's staff be warned by other symptoms? Will it only occur in conjunction with other more limiting substances?
>
> c) Risk assessment
> What is the probability of the substance occurring in *significant* concentrations? (which derives from both the historical record and some of the risk factors above) What would be the consequences if this happened? (which is a combination of the potential concentrations and the toxicity rating mentioned earlier).

Essentially the process is risk based, but pitched at an appropriate combination of judgement and quantification. It does not attempt to be a numerical analysis, and the amount of data and the wide variety of substances would not realistically support a more mathematical methodology.

Nothing is certain in human affairs, and nothing is final. Having carried out the categorisation process does not mean that the lists are then fixed for all time: any new sources of information, operating experience, toxicology or whatever, will trigger a review of a substance's Category. The list is also periodically reviewed to check for marginal cases and repeat examinations can be proposed if appropriate.

Assumptions

Carrying out this categorisation could not have taken place without a large body of reliable information on which to base the informed judgement parts. It presupposes that:

a) permissible concentrations are already known,
b) operating experience has been accumulated and is available to draw on,
c) that sound scientific, medical and engineering expertise is there to support the judgements made.

Exceptions

There are some limitations: the categorisation is not fully comprehensive. It deals with the vast majority of contaminants found in submarine atmospheres, but only covers those present in vapour or gas form. It does not deal with particulates and aerosols; and particular care is necessary in dealing with reactive or surface active substances, or short-lived substances.

Experience and Examples

Has the categorisation process made any difference?

It has enabled us to move substances to their appropriate category with reasonable confidence and so not to expend effort and resources unnecessarily on the pursuit of innocuous substances. It has illuminated instances where instrumentation of the required capability was not available to monitor some substances, and then justify a development programme to obtain suitable kit.

Some examples may best illustrate how it has worked:

> Category I: The list for continuous monitoring used to contain benzene. The records show clearly that this unpleasant substance, although routinely detected, is never present in sufficient concentration to present a health threat. Furthermore there are no sources of benzene on board in sufficient quantity to breach the limits. It is considered inappropriate to persist in continuous monitoring on-board but, because it remains a significant contaminant, routine retrospective monitoring is highly suitable and so benzene is placed in Category III.
>
> Category II: Some torpedoes contain Otto fuel as a propellant, the main constituent of which is a toxic nitrated ester. In normal circumstances this is contained within multiple barriers within the torpedo and none is present in the boat's atmosphere. But if a torpedo were to be damaged, there is potential for a release which would have to be dealt with by ship's staff with their resources on-board - it can't be left until the end of the patrol to find out what the exposures were. So continuous monitoring is not appropriate, but on-board real time monitoring is clearly necessary; hence Category II.
>
> Category III: A number of substances keep cropping up in significant quantities, but always well below MPC limits. They may come from many diverse sources in the materials of construction of the boat, or from equipment and systems on board.

Although they don't worry us yet, they need to be kept an eye on, in case adverse trends develop and positive action needs to be taken. Examples of these (and there are a large number in this Category) are such things as toluene, zylenes and naphthalene. Routine retrospective monitoring keeps tabs on these potential troublemakers.

Category IV: Marginal cases fall into this category: seldom found substances, or only ever present in low concentrations. There's no case to go routinely monitoring for them, but we need the capability to find them if we want to, and from time to time we feel we ought to check that their presence stays within bounds. There are a large number in this Category also: an arbitrary selection throws up carbon tetrachloride, methyl chloride, and carbon disulphide.

And finally Category V: the harmless ones; or the ones that are insignificant for other reasons. One example is acetic acid. It has a known toxicity, but the sailors are fond of it on their chips at mealtimes and common-sense indicates no problems have arisen as a result. Another, which requires rather more explanation, is hydrogen phosphide - phosphine. Why is this very toxic substance in Category V? It is because there is only one, very well understood source of it on board: it is present as an impurity in bottled acetylene. To release sufficient phosphine to create a health problem would require such a large release of acetylene as to pose severe problems of a different kind: and would be made obvious to ship's staff well before the phosphine content became a problem. For very good reasons use of acetylene on board is very tightly controlled. Taking all these factors into account it is considered too far-fetched to postulate a combination of circumstances which could lead to the phosphine itself being the significant hazard. So monitoring for it is of no value: other things will warn ship's staff of its presence and limit the submarine atmosphere first.

Conclusions

A new system of categorisation has been devised for substances found in submarine atmospheres.

The objective has been met, which was to develop a system of categorisation that has a rational basis and is also manageable, practical and able to command general support.

It is straightforward to apply, and assigns substances to one of five Categories by a risk assessment process.

The Categories have proved a useful guide to priorities in both toxicology assessment and in development of instrumentation.

Acknowledgements

I have received valuable support from all my colleagues in the UK submarine air purification community; it may seem invidious to single out anyone for individual mention, but I will do it anyway: Paula Dibben's sterling qualities have made what could have been hard work feel much easier, by her unique blend of first class advice and the panache she brought to her work. Francesca Durbin stepped in at very short notice and prepared the diagrams.

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Managing air quality and setting exposure limits for RN submarines

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ABSTRACT

As well as the major gases (O_2, CO_2, N_2, CO) the submarine atmosphere contains trace concentrations of a large number of organic contaminants that arise from a variety of sources. Although air purification devices embarked for this purpose remove these contaminants, an equilibrium steady state is reached during the dived period and the men breathe this cocktail of trace contaminants throughout the patrol duration.

These residual atmospheric contaminants must be monitored to ensure that the ambient concentrations are maintained 'as low as reasonably ***practicable***' (ALARP) and that any variations from the norm are recorded and suitable corrective action taken. Real-time monitors are embarked to record ambient concentrations of the critical gases, and also trends in organic contaminants. Adsorption tubes are provided to take regular air samples for retrospective analysis at a shore based laboratory. An inventory of organic compounds typically found in submarine air has been used to produce a list of target compounds, which are required by the RN medical experts to be routinely quantified for each patrol.

A simple method of sampling the air using custom-made Tenax tubes is used to pre-concentrate the contaminants prior to laboratory analysis. The concentrations of the target compounds are recorded on a database for assessment and medico-legal purposes. In addition, to enable the close control of the critical contaminants, action levels must be set to enable decisions to be made in real-time on compounds likely to have an acute effect on submariner health and performance.

Consideration must also be given to compounds posing a possible longer-term risk to health, which can be more suitably monitored post-patrol. Limits for submarine contaminant control have been set based on current UK and international occupational exposure standards. It was considered more appropriate to apply action levels, known as maximum permissible concentrations (MPC), to those compounds likely to impair submariners' performance, and to keep time weighted average continuous exposure standards (CES) for compounds likely to have longer-term health implications. This paper presents the concepts behind the standards and the regimes adopted by the RN for monitoring the trace organic contaminants.

INTRODUCTION

To maintain physical and mental health of the submariners operating the submarine as a fighting platform, atmosphere monitoring and control must ensure that good quality air is constantly available. The environment in the submarine may be considered to be a trapped bubble of air, subject to degradation due to the activity of the crew and the pollutants emitted by onboard machinery and materials. One of the major contaminants is carbon dioxide, which arises mainly from crew respiration. Tobacco smoking, cooking processes and hot machinery oil give rise to carbon monoxide and aerosols. Hydrogen is evolved during battery charging, and many organic vapours outgas from painted surfaces, polymer materials and adhesives. Chemicals may also arise from leaks in refrigeration equipment and chilled water systems.

Control of the contaminant concentrations within the enclosed environment is achieved by both passive and active techniques. Passive control is exercised by limiting both the materials used in submarine construction and the quantities and types of stores to be carried to certain permitted formulations(1). Equipment for active air purification(2) is embarked on all RN submarines to control ambient concentrations of the most important gases, eg oxygen production and carbon dioxide removal. Additional purification techniques control the concentration of organic vapours, carbon monoxide, etc and the methods are tabulated in Figure 1.

CONTROL OF COMPOUND	METHOD OF CONTROL
O_2 PRODUCTION	ELECTROLYSIS OF WATER
CO_2 REMOVAL	REVERSIBLE REACTION WITH MONOETHANOLAMINE
CO REMOVAL	CATALYTIC OXIDATION ON HOPCALITE (CuO/MnO_2)
H_2 REMOVAL	CATALYTIC OXIDATION ON HOPCALITE (CuO/MnO_2)
FREON REMOVAL	CATALYTIC DECOMPOSITION ON ALUMINA
ORGANIC VAPOUR REMOVAL	ADSORPTION ONTO CHARCOAL FILTERS
AEROSOL REMOVAL	ELECTROSTATIC PRECIPITATION

Fig 1. Submarine Air Purification Techniques.

Safe limits must be set both for the major respirable gases and for the many trace contaminants, which will be present in the atmosphere. Action levels at which the submarine crew must respond to remain within the 'safe limits' have been set. These are referred to as Maximum Permissible Concentrations (MPCs) and Figure 2 shows the MPC values(2) for some of the more important gases.

Moreover, Figure 2 demonstrates the range of concentrations which require monitoring, varying from per cent levels for oxygen and carbon dioxide, to parts per million by volume (vpm) for carbon monoxide and organic species. A variety of monitoring techniques is therefore required to ensure that these compounds can be analysed in admixture in submarine air, enabling a check to be made on whether MPCs have been exceeded. Regular atmosphere monitoring also provides feedback to the crew that the air purification equipment is functioning efficiently or indicates whether some remedial action is required.

COMPOUND	MPC 90 DAYS EXPOSURE	MPC 24HRS EXPOSURE	MPC 60 MINS EXPOSURE
OXYGEN	18% - 22%	18%-22%	18%-22%
CARBON DIOXIDE	1.0%	3%	3%
CARBON MONOXIDE	15vpm	200vpm	200vpm
HYDROGEN (Explosive Risk)	2%	2%	2%
R12 & R114	500vpm	1000vpm	2000vpm
R134a	250vpm	500vpm	500vpm
TOTAL ORGANICS	7.5vpm	10vpm	10vpm
TOTAL AEROSOLS	0.5 mg/m^3	None	None

Fig 2. Maximum Permissible Concentration for Selected Compounds.

Every UK nuclear submarine is equipped with a central atmosphere analyser, based on a mass spectrometer, to monitor these critical gases. In addition to the central analyser there are also portable monitors for individual contaminants, which are used as a back-up for monitoring in locations inaccessible to the main analyser, and also for species which are precluded from being monitored by the mass spectrometer. The commercial market is often able to supply equipment to fulfil these functions, but where no suitable monitors are available DERA devises solutions.

Some species, for example trace organics, have the potential to be harmful to health in the longer term. Submarine air contains a cocktail of organic vapours with in excess of 150 components, typically at sub-vpm levels, most of which have been identified, and the chromatogram in Figure 3 illustrates the complexity of a typical mixture.

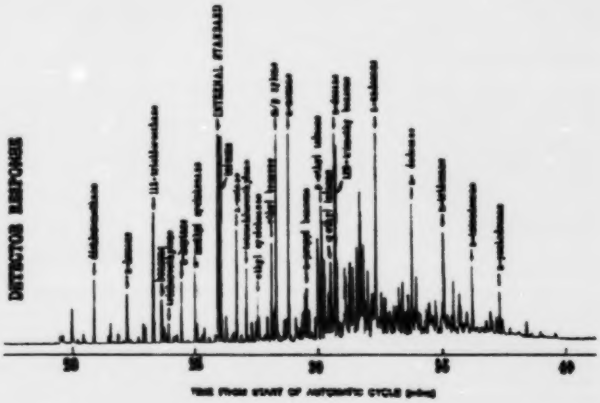

Fig 3. Chromatogram of Typical Airborne Organic Species.

There is no requirement to monitor all of these compounds in real-time although it is recognised that a record of submariner exposure is important for medico-legal purposes and to confirm compliance with passive air purification controls. The analysis of target compounds present in the organic contaminant mixture is performed by INM on samples collected during the patrol, using techniques developed by DERA which will be described later.

PRINCIPLES BEHIND SETTING EXPOSURE LIMITS FOR SUBMARINES

The advent of the nuclear powered submarine undertaking prolonged patrols without the requirement to bring in external air gave rise to the need to define levels of atmosphere constituents and contaminants that could be safely inhaled by the crew for the duration of a (submerged) patrol. Consequently, a set of submarine atmosphere exposure standards, the 'Maximum Permissible Concentrations', was developed for whole patrol duration designated MPC 90 days, and also for shorter excursions (MPC 24 hours and 60 minutes).

When the concept of Maximum Permissible Concentrations was introduced, there was no comprehensive, equivalent approach in use for occupational exposures in the UK, so the MPCs were set using the best available knowledge at the time. In a number of instances they were determined only after extensive research carried out by the Royal Navy, sometimes in collaboration with the United States and French Navies. Since then MPCs have been reviewed when there has been clear evidence in the literature that this was required. This approach was considered to demonstrate 'due diligence' from the medico-legal viewpoint. However, in more recent years there has been such a burgeoning of knowledge and Health and Safety legislation, that it was considered appropriate to introduce a more formal submarine atmosphere exposure standards setting and review procedure.

The MPC system was a forerunner of the present-day industrial occupational exposure standards, and it has been proven to work well in the context of the various scenarios within a submerged submarine. It is simple to use, being essentially a progressive set of 'Action Levels' requiring the crew to initiate corrective measures if certain maximum levels are exceeded or likely to be exceeded (the MPC 90, 24 and 60).

The MPC Action Levels are defined as:

Maximum Permissible Concentrations are Action Levels, which have been derived from health based submarine atmosphere exposure standards (the continuous Exposure Standard) used during submarine patrols. The MPCs may also take into account other factors such as deterioration in crew performance, engineering controls, operational constraints, socio-economic influences and the ALARP principle. If an atmosphere constituent or contaminant shows a rising trend, where possible, action should be taken to halt the trend before MPC is reached. If an MPC is breached specific action must be initiated to reduce the constituent/contamination to a level below the MPC 90.

MPC 90 days:

The maximum concentration which is acceptable for continuous exposure during a submarine patrol (approximately 90 days).

MPC 24 hours:

The maximum concentration that is acceptable for the crew to breathe for a 24 hour period. If the MPC 90 is breached but the concentration is between the MPC 90 and the MPC 24 the crew must reduce the concentration to below the MPC 90 within 24 hours.

MPC 60 minutes:

The maximum concentration that is acceptable for the crew to breathe for a 60 minute period. If the MPC 90 is breached but the concentration is between the MPC 90 and the MPC 60 the crew must reduce the concentration to below the MPC 60 within 60 minutes.

During the 1980s there was a requirement to document both the submarine atmosphere constituents and the rationale and methods for their control more (carefully). This was driven by the UK Health and Safety At Work Legislation. The methods of sampling and analysis for organics and aerosols were in need of improvement to allow for this more rigorous assessment, and a programme of work was initiated.

As part of this process, and as a natural evolutionary development, it was considered that a comprehensive review of submarine atmosphere exposure standards should be undertaken. This was achieved through the Royal Navy's connection with an independent medical body, the UK Medical Research Council (MRC).

The MRC's advisory committee favoured the use of the concept of time weighted average (TWA) exposure standards to be in keeping with UK legislation (EH40: HSW Act, etc). Additionally, it was proposed that the system be based on a series of risk assessments defining levels which would produce a minimum achievable risk for each substance. The RN decided, however, that a time weighted average system was too complex and time consuming to be managed throughout a submarine patrol. Additionally the need for a simple 'user friendly' set of 'action levels' to which the crew could respond in an emergency was a more practical approach and more likely to be used to maintain the ALARP principle. So it was decided that for the most important gases which required real-time monitoring, the MPC system would be maintained.

Compounds which required post-patrol monitoring could, however, be based on the TWA principle. These could be purely health based limits and it was recommended that these be designated Continuous Exposure Standards (CES), the definition being:

"A 24-hour time weighted average concentration that may be safely inhaled day after day for the duration of a submarine patrol lasting around 90 days."

The CES for each substance is determined by INM, wherever possible with a toxicological assessment being conducted before setting the standard. The Occupational Exposure Levels set by the HSE and other international bodies are also consulted and many of the CESs are set by dividing the HSE 8 hour TWA values[3] by a factor of 4 (assuming that the toxicological assessment confirms that this is a safe reduction factor). This calculation takes into account that the submariner is exposed to his working environment for 24 hours a day and 7 days a week for the patrol duration. The toxicological assessments are structured and documented in a specific format to aid uniformity, clarity and ease of updating. A database of the assessments is held at INM and a watching brief on the toxicology of the various substances is maintained. This is based largely on the literature circulated by the HSE and initiates an update of the CES if considered appropriate. As the HSE updates the EH40 document, the CES will also be reviewed and updated as required.

In parallel with the toxicological assessment, INM reviews the archived submarine atmosphere reports to determine the type of exposure experienced during past patrols. INM's Statistical Department has already developed a database for the substances presently monitored in real-time and is developing a database which will hold all retrospective atmosphere reports and enable a rapid and precise review of past exposure patterns. Combining the information gathered from the toxicological review and the post-patrol data enables INM to recommend that a substance be monitored in real-time or retrospectively.

PASSIVE CONTROL

To reduce the potential for introducing contaminants into the submarine atmosphere all materials to be used onboard must undergo a toxicological assessment prior to introduction into Service. This procedure is done by requesting full composition data from the manufacturer and then undertaking a review of the likelihood of release of components to the atmosphere and the hazards that release would cause. Items are then classified as 'free-use', 'limited-use' or 'banned'.

These categorizations are then promulgated(1) to the submarines, contracting authorities and stores organisations so that only appropriately approved materials should be used onboard.

REAL-TIME v RETROSPECTIVE MONITORING

Substances, which are recommended as requiring 'real-time' monitoring are allocated MPCs. The level set for each MPC is determined in the light of the individual CES toxicological assessment but requires the input of other specialists where appropriate (primarily the operators and the engineering services). The rationale behind setting the MPC levels is also documented and archived with the CES database at INM. Continuing with the present MPC Action Levels enables a further safety factor to be built into the system beyond that contained in the TWA approach.

The major compounds which require real-time monitoring and for which MPCs must be set comprise the major physiological gases for crew survival, ie oxygen, carbon dioxide, carbon monoxide, and the toxic products of equipment failure or emergencies, eg hydrogen, oxides of nitrogen, chlorine, amines and freons.

Compounds likely to have potential long-term health effects may be monitored post-patrol and therefore need to be sampled for retrospective analysis. These are as diverse as potential carcinogens (eg polycyclic aromatic hydrocarbons and benzene) or chemicals with deleterious mechanical effects (eg siloxanes as promoters of wear in brushes on electrical motors and generators). New challenges to the submarine atmosphere may also be targeted such as 'ozone friendly' halocarbons.

New substances discovered in the routine monitoring process, which may pose a risk to either health or function of the submarine, can also then be added to the target list.

METHODS OF REAL-TIME CONTAMINANTS MONITORING

Akin to the US Navy perspective, continuous monitoring is carried out from fixed sampling points using a Central Atmosphere Monitoring System (CAMS), based on a mass spectrometer with infrared analysis for CO. This is backed up by the use of single species portable monitors for routine comparison analysis and use in small or confined spaces.

Draeger tubes are used for single species and for fire and emergency monitoring, as they are simple to operate and may be used by personnel with limited training.

Submarines also carry a photoionisation detector, which is used as a non-selective method to assess total hydrocarbon contamination. It is a portable detector and is useful to survey various locations around the boat for leaks or other 'hot spots'. If higher than 'normal' concentrations are found then remedial action can be instigated. Similarly real-time aerosol monitoring is carried out routinely using a portable aerosol monitor, based on the light scattering principle. This monitor measures respirable aerosol mass concentration and, like the photoionisation detector, is suitable for assessing trends.

RETROSPECTIVE SAMPLING AND ANALYSIS OF CONTAMINANTS

Once the list of organic compounds targeted for quantification after every patrol had been selected, suitable sampling and analysis methods were reviewed. It was important to take account of the future strategy for collecting these atmosphere contaminants since this process would be completed by submariners. The chosen method would therefore need to be rapid, simple and able to be used reproducibly by non-scientific personnel.

Diffusion tubes available at the time were felt to be unsuitable for quantification of the targeted compounds since many of the diffusion coefficients needed for quantitation were unavailable.

Whole air sampling(4) into electropolished stainless steel cylinders was attractive but expensive for issue to the whole submarine flotilla. It was also rather more complex as a sampling regime for the submariners to use.

Adsorption tubes(5-7) were decided to be the simplest approach and were ideal for low concentrations of contaminants, since this method pre-concentrated the mixture, thereby allowing better analytical limits of detection. Submariners were already familiar with using Draeger detector tubes and the method of collection using adsorption tubes was similar. One of the practical issues with the use of adsorption tubes was that those commercially available were not sufficiently well sealed to prevent further ingress of contaminants after sampling and before analysis. The time interval between sample collection and laboratory analysis was likely to be measured in months and the problem was to ensure sample integrity during this period.

DERA designed a glass adsorption tube compatible with industry standard analytical thermal desorption equipment and able to be sealed by fusing the glass ends after sampling. Figure 4 illustrates the custom made Tenax tube and the modified Draeger pump.

Earlier trials had demonstrated that the ambient concentration of organic compounds was low, and it was considered an advantage to employ an adsorbent which could preconcentrate them. The majority of the targeted compounds were hydrocarbons and other organics amenable to efficient collection on Tenax adsorbent without loss, if a small sample volume of air (200ml) was taken. The Draeger pump was used to collect the sample as this fulfilled the criterion of being simple to use and had the added advantage that submariners were familiar with it.

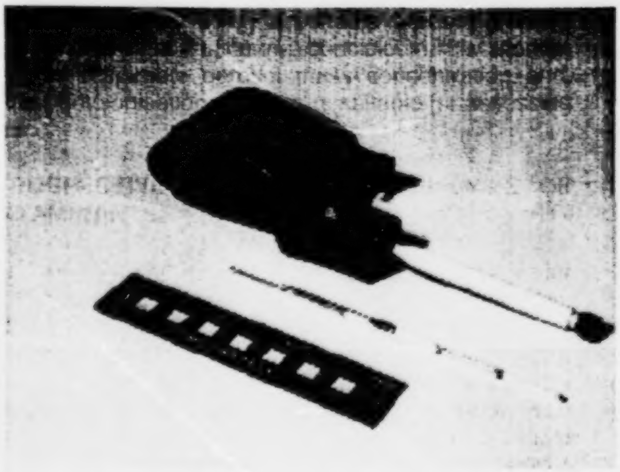

Fig 4. Tenax Adsorption Tube and Sampling Pump.

Each submarine carries Tenax tubes, Draeger pump and a small hand held butane torch, which is used to reseal the ends of the glass tubes after the sample has been taken. The protocol is to take air samples at regular locations and times throughout patrol. At the end of the tour of duty the tubes are dispatched to INM for analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) and recording of the targeted compounds. This information is then posted to the ***relevant Submarine*** Squadron.

If higher than 'normal background' concentrations are indicated by the photoionisation detector or the aerosol monitor during the patrol, then additional Tenax tube samples will be taken for subsequent assessment of the problem at the shore based laboratory.

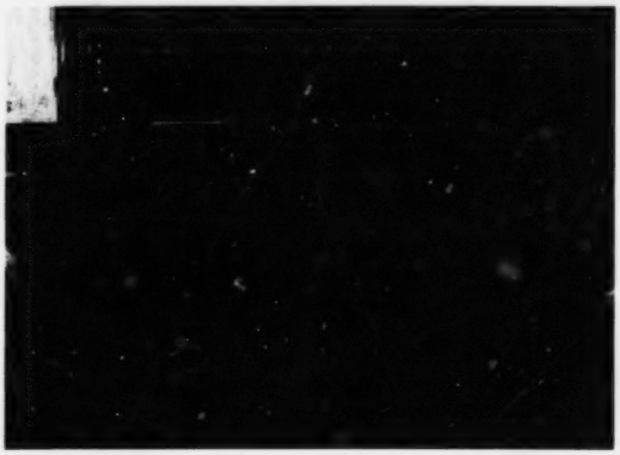

Fig 5. The laboratory analytical equipment (TD/GC/MS).

CONCLUSION

This system of managing the submarine air quality by atmosphere control and monitoring has allowed the concentrations of contaminants to be monitored regularly and provided the assurance that good quality air is being maintained. It has also provided the records required for confirming compliance with RN atmosphere control policy and for medico-legal purposes and gives confidence to the crews that their well being is important. Additionally, submariners have become more aware of environmental issues, perhaps partly as a result of their greater involvement with sampling procedures, and have become more proactive and careful to reduce their contributions to atmosphere contamination to a minimum.

However, it is prudent to review the inventory of atmosphere contaminants from time to time to provide the confidence that new compounds are not arising in the submarine atmosphere. Additionally, new information on contaminating species must be reviewed to ensure that any new toxicological studies are taken into account when reviewing the target compound list. Further developments under discussion include broadening the capture range of the Tenax adsorbent and tightening controls on contaminants with potential facto-toxic effects.

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RN SUBMARINE ATMOSPHERE MONITORING – RETROSPECTIVE ANALYSIS

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Introduction

Following the completion in 1963 of the Royal Navy's first nuclear-powered submarine, HMS DREADNOUGHT, it was decided that retrospective analysis of the atmosphere onboard nuclear submarines of the Royal Navy was an essential requirement. This was because the nuclear reactor enabled the boat to stay submerged almost indefinitely, unlike conventional submarines which have to return to the surface at predictable times to recharge their batteries by running their diesel engines. There was the potential, therefore, for toxic contaminants to gradually build up within the nuclear submarine's atmosphere when submerged for long periods of time but this could be checked upon by taking samples of the atmosphere for retrospective analysis and ensuring that the levels of contaminants do not exceed permitted levels. Retrospective analysis has thus been carried out on a routine basis onboard Royal Navy submarines since around 1965.

This has been achieved by members of the submarine's crew taking samples of their submarine's atmosphere onto adsorptive media at specified intervals and locations during a submarine's patrol and whenever an unusual incident has occurred onboard, such as after a chemical spillage, for analysis at the end of the patrol.

However, submarine atmosphere sampling initially carried out in the 1960s was somewhat different than that which is carried out today.

This paper aims to give a history of almost 40 years' atmosphere sampling in Royal Navy nuclear-powered submarines from HMS/Ms DREADNOUGHT, the 'early' VALIANT class (comprising VALIANT and WARSPITE) and the RESOLUTION class (the Polaris boats) of the 1960s, the 'later' VALIANT class (CHURCHILL, CONQUEROR and COURAGEOUS) and the SWIFTSURE class of the 1970s, the TRAFALGAR class of the 1980s and the VANGUARD class (the Trident boats) of the 1990s.

The early days

From its beginning in the middle 1960s until the early 1970s, sampling on submarines, such as DREADNOUGHT through to COURAGEOUS and CONQUEROR, was limited to organic vapour samples collected by activated charcoal and aerosol samples collected onto filter paper. The organic vapour samples were subsequently analysed by solvent extraction and gas chromatography to determine levels of benzene, toluene, total xylenes, C8 and C9 aliphatics, and C9 aromatics. The aerosol samples were subsequently analysed for total aerosol content by gravimetric analysis, for total organic aerosol content by extraction of the filter paper with benzene, which gave an estimation of levels of mineral oil in the submarine atmosphere, this benzene extract being further analysed by gas chromatography to quantify the aliphatic, the aromatic and the oxygenated organic compounds present.

The earliest complete report found by the authors was for the analysis of the trace contaminants from the atmosphere of HMS DREADNOUGHT in May 1965, when closed-boat conditions were maintained for approximately 15 days and samples were collected over the period 140 to 280 hours from the start of submergence.

The levels of the few contaminants monitored for appear to have been compared against maximum levels that had been recommended by the Medical Director General (Navy). These have developed into the submarine maximum permissible concentrations (MPCs) that remain in use today and are published in the Royal Navy's BR1326 'Air Purification in Submarines'.

The sampling method for organic vapours used onboard DREADNOUGHT in 1965 was practically identical to that used until very recently as the submarine's atmosphere was drawn through 100grammes (g) of dry, activated charcoal for 12 hours at a flow rate of about 35 litres per minute (lpm). The sampling method for aerosols, however, was somewhat different in that DREADNOUGHT's atmosphere was drawn through glass fibre filter papers for 12 hours at air flow rates of about 570 lpm (ie 410 cubic metre (m^3) sample), whereas today a flow rate of 700 lpm is used for a 24 hour time period (ie 1000 m^3 sample).

Analysis of the charcoal samples indicated that the hydrocarbon concentrations in the atmosphere onboard DREADNOUGHT were within the range 33 to 61 milligrammes per cubic metre (mg/m^3), with an average of 44 mg/m^3. The maximum level recommended at that time by the Medical Director General (Navy) was 40 mg/m^3. However, if uncertainties regarding desorption efficiencies were taken into account, then the report concluded that the average concentration of hydrocarbons could be increased to 78 mg/m^3. The analytical laboratory report on the DREADNOUGHT results commented that:

> "For comparison, values given in American reports for concentrations of hydrocarbons determined from…charcoal exposed on U.S.N. nuclear submarines, are currently about 2 mg/m^3. This indicates the considerable success in "housekeeping" achieved, in particular, in connection with the restriction on the use of sources of organic solvents. R.N. failure at present in this field is shown by the considerable concentration of xylene found in the atmosphere. It must be assumed that the xylene is evolved from paint and/or paint solvents."

About 70%(w/w) of the desorbates were aromatic, with xylenes predominating at about 35%. Other specific aromatics looked for were benzene, toluene, methyl ethyl benzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and isopropyl toluene (p-cymene). The remaining 30% of the desorbates were C_6 to C_8 aliphatic compounds.

Analysis of the filter papers, which had all been exposed in the Upper Level Machinery Space, indicated that the average concentration for aerosols was 0.2 mg/m^3 (range 0.17 to 0.30 mg/m^3). The benzene soluble material was about 65%(w/w) of the total aerosol and this was made up mostly of aliphatics. It was considered that the aerosols were predominately from lubricating oils, in contrast to those in American nuclear submarines which were from tobacco smoke. A level of 0.2 mg/m^3 of aerosol was regarded as satisfactory and the comment was made that this could probably only be reduced if larger electrostatic precipitator capacity was installed in the submarine.

The analytical laboratory supporting the Royal Navy's nuclear submarine retrospective atmosphere monitoring programme at this time was located within Rosyth dockyard, Scotland.

The early 1980s

By the early 1980s, improvements in analytical techniques, together with an increase in the number of materials for which submarine MPCs had been derived and published in BR1326 due to wider recognition of the potential contaminants present in a submarine's atmosphere and improvements in toxicological research, meant that the number of compounds routinely looked for during the retrospective analysis of the charcoal samples was as follows:

- Total hydrocarbon content;
- Individual levels of the following aromatics - benzene, toluene, ethylbenzene, total xylenes, cumene, n-propylbenzene, o-ethyltoluene, m-ethyltoluene, mesitylene, p-cymene, pseudocumene, 1,2,3-trimethylbenzene, p-dichlorobenzene;
- Total aromatics (as toluene);
- Total aliphatics (as hexane);
- Total significant unknowns.

The analytical laboratory moved from Rosyth in 1988 when the dockyard was privatised as it was felt essential that the laboratory should remain under Ministry of Defence authority. Its new location was at Eastney in Portsmouth where it came under the auspices of the Portsmouth dockyard laboratory.

The early 1990s

In addition to determining the total aerosol of the submarine atmosphere, the filter papers were now analysed for metals and examined under the microscope to identify the range of fibrous and particulate matter present.

A new organic vapour monitoring technique, which had been extensively evaluated by what is now DERA Haslar, was introduced to ultimately replace the charcoal sampling method.

The primary requirements of the new monitoring technique were four-fold:

- Ability to adsorb more organic species than charcoal;
- Automated analysis;
- Much lower detection limits enabling far shorter sampling times;
- Easy to use on board a submarine by the crew;

These requirements were realised by utilising Tenax TA - a porous polymer adsorbent designed to collect organic vapours with a boiling range of 100°C - 400°C and molecular size range n-C_7 to n-C_{26} (although excellent results are also obtained for C_6 benzene). Instead of each sample being collected over a 12 hour period, the much quicker and more flexible Tenax system meant that samples could be taken over a matter of minutes, making it far easier to take multiple samples of the submarine's atmosphere, especially after an unexpected event, such as a chemical spillage, at the site of the event. The introduction of Tenax packed into sealed sampling tubes, which are opened for sampling and then sealed again to prevent ingress or egress of organic vapours, also meant that the labour intensive retrospective analysis and potentially hazardous chemical desorption of organic materials collected onto charcoal could be replaced by automated thermal desorption. The submarine atmosphere was drawn through the Tenax tube using 2 strokes of a bellows pump (total sample of 200 ml) already carried on board for monitoring certain gases in the event of a fire. This meant that training the crew to sample using the Tenax tube was very simple as it involved equipment with which they were already familiar.

Tenax sampling was introduced in 1995 and carried out in tandem with charcoal sampling so that results from the 2 organic vapour sampling methods could be compared.
With the closure of Portsmouth dockyard laboratory in 1992, the submarine analytical laboratory came under the control of the Institute of Naval Medicine (INM) in Gosport but remained at Eastney until a new suite of laboratories had been built at INM. In 1998, the analytical laboratory moved across Portsmouth Harbour to its current location within INM.

Today

Coming right up to date, current routine monitoring reports the following with respect to aerosol samples:

- Total aerosol content (by gravimetric analysis);
- Individual levels of the following metals - antimony, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, tin, titanium, vanadium (qualitative analysis by inductively-coupled plasma (ICP) spectrophotometry with mass selective ion detector (MS));
- Total toluene-soluble material to estimate levels of hydraulic/lubricating oils (gravimetric by accelerated solvent extraction (ASE));
- Individual levels of the following water-soluble anions - fluoride, chloride, chlorate, nitrite, nitrate, bromide, sulphate, phosphate (qualitative analysis by ion chromatography (IC));
- Microscopic evaluation of fibres and particulate matter as collected.

The excellent trial results produced by the Tenax sampling regime resulted in the UK Ministry of Defence's Submarine Atmosphere Purification Committee agreeing earlier this year that charcoal should no longer be used and so Tenax is now the only adsorbent for sampling organic vapours within a Royal Navy submarine's environment. The organic vapour samples are routinely analysed for:

- Carbon disulphide, n-hexane, butan-2-ol, 2-butanone, ethylacetate, chloroform, 1,1,1-trichloroethane, methoxyethanol, butan-1-ol, carbon tetrachloride, 1,2-dichloroethane, benzene, methoxypropanol, trichloroethylene, ethoxyethanol, 4-methyl-2-pentanone, toluene, 2-hexanone, 1,1,2-trichloroethane, tetrachloroethylene, 1,2-dibromoethane, tetrachloroethane, ethylbenzene, total xylenes, butoxyethanol, ethoxyethylacetate, styrene, total ethyltoluenes, total trimethylbenzenes, 1,4-dichlorobenzene, naphthalene, 1-methylnaphthalene (quantitative analysis by thermal desorption followed by GC/MS);
- Levels of unknown organics are estimated semi-quantitatively by the software against the internal d8-toluene standard and reported as a total figure. The software is also able to make a 'best-guess' to suggest possible candidates for these compounds. Such compounds routinely 'found' are reported as: methylbutane, ethanol, 2-methyl-1,3-butadiene, isopropyl alcohol, 2-propanal, isocyanomethane, acetic acid, 2-butenal, 2-methylpropanol, cyclohexane, heptane, methylcyclohexane, 1,2-ethandiol, octane, nonane, octamethyltetrasiloxane, decane, phenol, benzaldehyde, limonene, undecane, acetophenone, dodecane, benzoic acid, benzenediol, dimethylethylphenol.

Comparing one of the most recent retrospective analysis reports with that from DREADNOUGHT in 1965 revealed that levels of contaminants have improved over the years. The level of aerosols in the atmosphere of today's submarine has reduced to about one-third of 1965 values to 0.05 - 0.11 mg/m^3 (Current $MPC_{90} = 0.5$ mg/m^3), with lubricating and hydraulic oils still the main sources. Total organics present in today's submarine atmosphere have reduced to about one-fifth of 1965 values to 6.8 – 15.2 mg/m^3 (Current $MPC_{90} = 40$ mg/m^3, exactly the same value as in 1965), with solvents from paints, adhesives and sealants, and organic vapours from diesel, hydraulic and lubricating oils, remaining the main sources.

Trends

The results of retrospective analyses are used for 2 purposes:

- to check compliance with MPCs for the patrol during which the samples were taken;
- to indicate trends within a submarine's atmosphere over a period of time.

The results available over the last 35 years have been examined for any such trends and these can be summarised, as follows:

1. MPC excursions used to be frequently encountered but are now rare events;
2. atmospheric quality decreases in proportion with the length of the patrol;
3. atmospheric quality decreases in proportion with the age of the submarine;
4. good maintenance of air purification systems during a patrol is the most important factor affecting atmospheric quality. This will also have an affect upon 2. and 3.

The Future

As new materials are introduced (eg with the future ASTUTE class of submarine), the number of compounds that need to be looked for routinely in the retrospective samples is likely to increase.

Siloxanes are likely to require more careful monitoring. At present, only 2 are currently found in the atmosphere onboard RN submarines and, although these appear to have no adverse health effects upon the human body and there is thus no toxicological reason to monitor for them, they have a major effect from the engineering viewpoint as their presence in the atmosphere is thought to cause advanced brush wear in electrical equipment. INM's analytical laboratory is developing techniques to quantify siloxanes.

SPACECRAFT MAXIMUM ALLOWABLE CONCENTRATIONS FOR AIRBORNE POLLUTANTS.

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Abstract

During the last decade the Toxicology Group at Johnson Space Center (JSC) has worked with the U.S. National Research Council Committee on Toxicology (NRCCOT) to set and document the rationale for Spacecraft Maximum Allowable Concentrations (SMACs) for astronaut exposures during missions. The SMACs are set for continuous exposure periods of 1 hour to 180 days. The values established for SMACs affect the offgassing permitted from hardware and materials, the level of containment of hazardous compounds, the design capacity of the air revitalization system, and the implementation of flight rules. Since the SMACs affect many as+pects of human space-flight, they must be set with the utmost credibility. There is no merit in setting irrationally low SMACs because these will result in unnecessary expenses; however, the SMACs must be set to achieve an acceptable level of control of the risk of health effects from airborne pollutants. The process of setting SMACs for a compound begins with a literature search by one of the JSC toxicologists. Key documents are obtained, translated if necessary, and reviewed for quality and compatibility with any similar studies. A document is created describing the toxicological database, identifying significant toxicological effects, and presenting a thorough rationale to support proposed SMAC values. This document is presented to the NRCCOT members for critical review, and they can accept the document and SMACs, or make recommendations for changes or additions. The process continues until an agreement is reached that the SMACs are appropriate and the documentation supports the values set. The success we have had with this process is due to several factors. The membership of the committee includes established experts in a variety of toxicological disciplines, there is a flexible framework for setting SMACs, and there is an open dialogue between the creator of the document and the expert reviewers. This process has resulted in SMACs for approximately 60 compounds that have the potential to pollute spacecraft atmospheres. Many of these pollutants are also found in submarine atmospheres; however, a SMAC may not directly apply to submarine atmospheres if factors for space-flight induced physiological effects have been included in the derivation of the SMAC. Furthermore, the SMACs are set to protect to certain risk levels that are acceptable to NASA, but a different level of risk may be acceptable to operators of submarines. A summary of SMACs and the limiting toxicological effects can be found in JSC 20584; the complete documentation resides in 4 volumes from the U.S. National Academy Press. The summary document and volumes can be accessed through the JSC Toxicology Group web site, which is located at http://www.jsc.nasa.gov/toxicology.

Introduction

Standards have been set for human exposure to many airborne pollutants by many organizations and for many applications. Inspection of these standards will show that they can range over orders of magnitude even when the applications seem similar. Furthermore, air quality standards are frequently updated to reflect new approaches to risk assessment and the availability of new data; hence, standards only a few years old can be seriously outdated. Historically, air quality standards for U.S. space vehicles and U.S. submarines have been established by the National Academy of Sciences or the National Research Council (NRCCOT, 1988; NRCCOT, 1984-7; NAS, 1968; NRCCOT, 1972). In preparation for the era of the Space Station, NASA began a cooperative effort with the NRCCOT in 1989 to set and document air quality standards for long-duration stays aboard space vehicles such as the International Space Station. NASA was also working on instruments capable of providing real-time air quality assessments during accidental releases, hence, standards for short-term exposures were set to guide flight controllers in the event of a contingency in which real-time instruments were providing pollutant measurements. The process for setting these spacecraft maximum allowable concentrations (SMACs) begins when a Johnson Space Center (JSC) toxicologist prepares a document reviewing relevant literature and giving a rationale for SMACs for exposures of 1 hr, 24 hrs, 7 d, 30 d, and 180 d. The rationale is based on flexible guidelines given by a subcommittee of the NRCCOT (NRCCOT, 1992). The author of the document defends it before the subcommittee, which gives concurrence with the document or direction for changes in the document. After additional NRC reviews, the documents are published by the National Academy Press (NRCCOT, 1994-2000).

Approach

Anyone considering use of air quality standards must look for a number of quality factors inherent in the approach used to set and document the standards. The group setting the standards should be as free of bias as possible and have established expertise in all relevant toxicological disciplines. The population for which the standards are being set should be well defined. The level of risk to be tolerated for both carcinogenic and non-carcinogenic endpoints should be explicitly known and accepted by those involved in the process. The documentation should demonstrate a thorough review of the literature, an evaluation of the quality of key studies, and an explicit rationale for the standards in question. The rationale employed should be consistent from one compound to the next and should use scientific evidence rather than "uncertainty factors" whenever possible. Key studies that seem to provide conflicting data must be compared and evaluated for quality.

The JSC toxicologists who supervise the literature search, write the documentation, and propose initial values for SMACs are doctoral-level individuals with expertise in inhalation toxicology or genetic toxicology. Most are board-certified in general toxicology by the American Board of Toxicology, Inc. The NRCCOT subcommittee that reviews the documents and standards includes experts in inhalation toxicology, neurotoxicology, pharmacokinetics and metabolism, genotoxicity, reproductive and developmental toxicity, epidemiology, and statistical risk methods.

The target population for protection by NASA is, of course, astronauts. These are healthy individuals generally between 35 and 60 years of age, who have been thoroughly tested for any conditions that would affect their ability to participate in demanding space activities. Astronauts are not expected to be pregnant or become pregnant during flight so developmental toxicity endpoints are not considered pertinent in setting SMACs. Astronauts do experience a number of biochemical and physiological changes that could make them more susceptible to certain types of toxic insult. Astronaut-specific factors are used in setting SMACs for hemtotoxicants, immunotoxicants, cardiotoxicants, and radiomimetic compounds. Astronauts experience a 10% loss of red cell mass within the first few days of flight, they undergo a number of changes in their immune systems, they are more susceptible to cardiac rhythm disturbances, and they are often exposed to higher radiation levels than they would experience on earth (Nicogossian et , 1994).

Launching humans into space and sustaining them there for long periods of time is an inherently risky enterprise. The key to success is to manage each risk to appropriate levels without expending unnecessary resources to mitigate trivial risks. Carcinogens that behave in the traditional way, that is they seem to follow a linearized model, are permitted to be no higher than concentrations that pose a 1/10,000 excess risk of cancer with a 95% confidence. Certain carcinogens (e.g. furan, isoprene) seem to follow a threshold model in which case the SMACs are set to be fully protective of any risk of cancer. That is, the limits are set securely below the threshold that could lead to cancer. For non-cancer endpoints the acceptable level of risk can be fairly high (1/10) for minor effects (e.g. mild headache or eye irritation) that could occur as a result of brief exposures. This concept is applied to setting SMACs for exposures of 1 or 24 hours. These short-term SMACs are for management of contingencies only. For more serious effects (e.g. CNS depression) and longer exposures the risk is managed to levels approaching 1/1,000, which is viewed as essentially no risk given the small number of astronauts who fly at one time.

Uncertainty Factors and Relevancy of Animal Models

Uncertainty factors are default values to be used only in the absence of a scientific rationale for a SMAC. The default uncertainty factor of 10 has been applied for extrapolation from *the most sensitive* animal model to humans and for extrapolation of a lowest-observed-adverse effect level (LOAEL) to a no-observed-adverse effect level (NOAEL). No uncertainty factor is used for intraspecies variability because of the relatively homogeneous and healthy population, and no factor is used for inadequacy of the database. However, a factor of 10/sqrt (n), where "n" is the number of test subjects in a human study in which no adverse effect was noted, has been used. This factor compensates for the weakness in detecting effects when a small number of subjects is used. The default time extrapolation method is the so called Haber's Rule, which asserts that adverse effects will be the same if the exposure time is increased by a certain fraction and the concentration is decreased by the same fraction. This is used only in the direction of increasing exposure times, that is extrapolation of a subchronic exposure to a chronic exposure limit. The factors are combined in a multiplicative fashion, which can lead to some extremely large uncertainty factors. The scientific approaches to avoid meaninglessly large uncertainty factors are described below.

Interspecies extrapolations are appropriate only when the toxic effect observed in an animal model is relevant to human susceptibility. Certain toxic effects observed in animal models are known to be poor models of human susceptibility. One example is the renal calcification seen in guinea pigs exposed to 5,000 ppm carbon dioxide. We know from submariner data that humans do not exhibit this effect at low concentrations. Apparently guinea pigs mobilize bone calcium in response to elevated environmental carbon dioxide, whereas, humans do not (Wong, 1996). Nephropathy in male rats exposed to hydrocarbons for an extended period is not relevant to humans because humans do not produce the large amounts of alpha-2u-globulin necessary to facilitate the effect in male rats (Swenberg et al., 1989). Hormonally-mediated, thyroid injury observed in rodents is not applicable to humans because of the vast interspecies differences in hormone binding and half lives (McClain, 1992).

Scientific Tools

Assuming one has determined that a lesion or adverse effect found in an animal model is relevant or *may be relevant* to human risk assessment, how can scientific tools be used to avoid the default factor for interspecies extrapolation? The default factor of 10 is viewed as a combination of species differences in the absorption and delivery of active metabolite to the target tissue and the inherent susceptibility differences of the target tissue to toxic injury. An example using furan can be used to illustrate this concept. Rats are known to get liver cancer from prolonged exposure to furan; however, Kedderis and Held (1996) have estimated that during a 4-hour exposure to 10 ppm furan, rat liver is subjected to a 3 fold higher concentration of furan metabolites than human liver. This is primarily due to a 3-fold lower absorption (on a mg/kg body weight basis) in the respiratory system of humans compared to rats. This suggests that if humans are indeed more susceptible to furan than rats, it is due to higher tissue susceptibility in humans and not to greater absorption in humans. The species extrapolation factor was estimated at 3 for extrapolation of liver toxicity from rats to humans rather than 10.

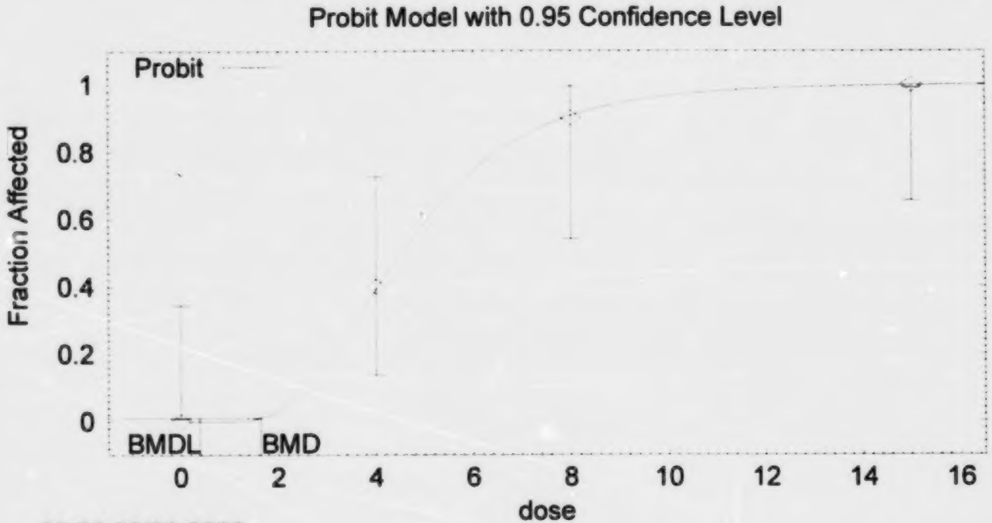
Dose-response extrapolations from moderate doses to very low doses are a classic problem in toxicology. Often animals are exposed to relatively high concentrations with no more than 50 animals per group. It is impossible to detect an increased risk of a few percent directly, so extrapolation from the high doses that impart a measurable increase in risk to low doses with an acceptable risk is a challenge. The default approach presumes that dividing the LOAEL by a factor of 10 will provide an estimate of the NOAEL. On the other hand, the NOAEL may be available, but from a study with 10 or less animals per group. Under these conditions we have tried to apply the bench-mark-dose (BMD) approach to estimate a true NOAEL. Again, furan will be used to illustrate this approach.

When rats were given furan by oral gavage 5 days per week for 13 weeks, biliary hyperplasia was noted in the incidences shown in the table 1. BMD is the central estimate of the dose that gives an increased risk of 10% or 1%, whereas, BMDL is the lower 95% confidence dose on the central estimate. The P value is an index of the goodness of the mathematical model fit to the incidence data. There are a number of controversies in the application of this approach. Foremost is the choice of model to use in predicting increased risk. In the example below, if the BMDL$_{01}$ were used for prediction, the estimate ranges from 0.03 mg/kg to 0.38 mg/kg with high P values for both models. The NRCCOT has determined that the BMDL$_{01}$ should be considered a true NOAEL, whereas, other groups (e.g. the U.S. EPA) have advocated the BMDL$_{05}$ or BMDL$_{10}$ as a surrogate NOAEL The argument is that the estimates at 5-10% are more meaningful since experimental data are often available in this incidence range and almost never in the range of 1%. As illustrated below, the 10% numbers are less sensitive to choice of model.

Table 1. Biliary Hyperplasia in Rats Given Furan for 13 weeks-Bench Mark Dose Analysis

Dose	Incidence		Doses Giving Predicted Incidence According to Models					
			log Probit Model		Logistic Model		Gamma Model	
(mg/kg)	Measured	Predicted	BMD	BMDL	BMD	BMDL	BMD	BMDL
0	0	10%	2.57	0.99	2.24	1.21	2.29	0.41
4	4							
8	9	1%	1.63	0.38	0.46	0.15	1.16	0.03
15	10	FIT>	P = 0.98		P = 0.80		P = 0.99	

The figures below illustrate the tabulated BMD approach for the log probit model, the logistic model, and the gamma model, all with reference to a 1% increase in risk. Note that the curves all give a good fit to the data; however, the predictions for the dose giving a 1% increased risk are highly variable.



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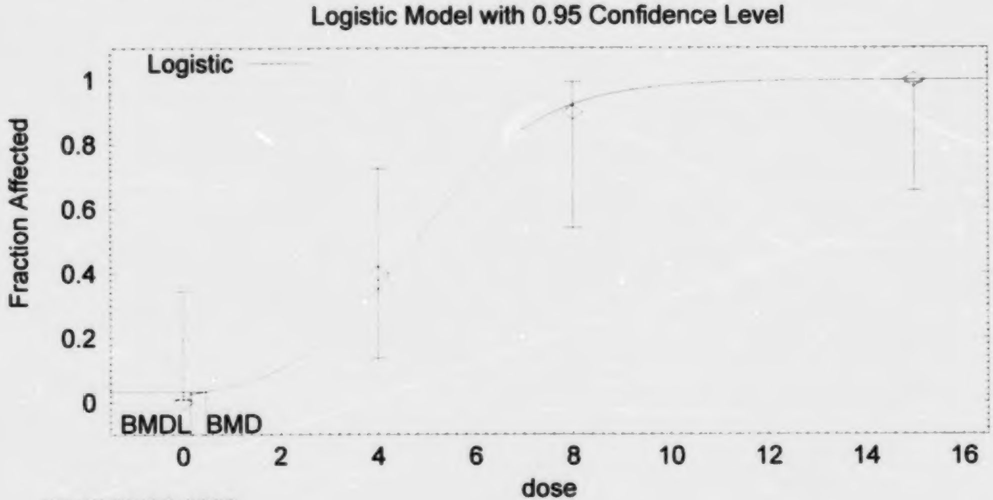

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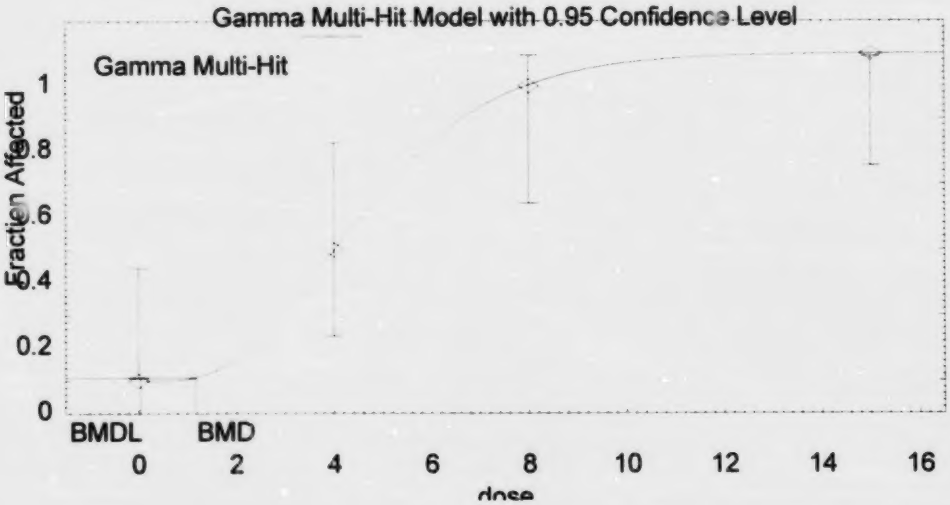

Intraspecies factors are not included because the astronaut population is relatively homogeneous and healthy. Under some conditions there are genetic differences in a healthy population that are likely to make certain persons more susceptible to toxic effects from pollutants. One example is ethanol which elicits a "flushing response" in persons, primarily of Asian ancestry, who consume relatively small quantities. This response is due to an allele which leads to production of a form of aldehyde dehydrogenase which is much less capable of removing the acetaldehyde formed during the metabolism of ethanol. The accumulation of acetaldehyde is associated with the flushing response. To address this more susceptible population, a limit was set for ethanol inhalation that keeps blood alcohol level below the threshold associated with flushing in susceptible persons.

Exposure-time extrapolations are often a problem for risk assessment. For many compounds only subchronic data (typically 13 week exposures) are available, yet a limit for chronic exposures is needed. Under some conditions one can show that a threshold concentration has been reached below which no toxic effect occurs no matter how long the exposure. For indole a threshold inhalation concentration was chosen as a NOAEL for long exposures because at that concentration the body's normal load of indole would be increased by less than 5%. The default approach, which is Haber's Rule (k=ct, where k is a constant effect, c is the concentration, and t is the exposure time) can be refined to the equation $k=c^a t^b$ (ten Berge et al., 1986); however, it is rare that sufficient data are available to determine the exponents 'a' and 'b' so that extrapolations can be made.

A final issue that deserves mention is the treatment of mixtures of compounds. NASA has taken the approach advocated by the TLV^R Committee (ACGIH, 1998) in which compounds that act similarly are added together in proportion to their exposure limit. The equation NASA uses is as follows:

$T_{group} = SMAC_1/C_1 + SMAC_2/C_2 + \ldots SMAC_n/C_n$, where there are n compounds in the group.

The air is considered acceptable when each T_{group} is below 1. The difficulty with this approach is knowing exactly which compounds belong in each toxicity group.

Conclusions

Obviously, setting exposure limits is an imprecise exercise. The best one can achieve is a consistent approach to the assessment and an explicit rationale for the limit that experts accept. Each limit constitutes a hypothesis: if the concentration is maintained below the specified limit, then humans breathing the air for a specific amount of time will not experience a toxic effect. If the limit were set much higher, then some small portion of people would experience toxic effects. Such hypotheses will never be tested for ethical reasons, so the debates over which approach is best and how scientific information can be used will continue with no end in sight.

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AN AIR QUALITY ASSESSMENT ONBOARD AN OBERON CLASS SUBMARINE- HMCS OKANAGAN

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Introduction

To assist in the development of management plans for future submarine air quality initiatives prior to the Canadian Navy's move to a new submarine, DCIEM was asked to re-examine air quality to determine if the atmosphere complies with the Standard, BR 1326 (OOS), *Air Purification on "O" Class Submarines* (1). Engineering modifications and alterations to atmospheric procedures and policies implemented since the last habitability assessment of 1987 (2), deemed it appropriate to assess the effectiveness of these changes on ventilation and air quality from a submariner health and safety context in an Oberon class submarine.

As well, although Canada's Navy will soon include a new class of submarine, a habitability trial on an Oberon class was warranted since the information gained would be readily transferred to the new Victoria class (3). Both classes of submarines are diesel operated, the method of cleansing and upgrading the atmosphere is identical (Oxygen candles and Carbon Dioxide scrubbers), and the relative position of candles and scrubbers is the same. Moreover, and most important, the mission operations and the Standard Operating Procedures (SOP's) onboard the Oberon's would be migrated to the new class.

In order to achieve the many management objectives which address potential procedural and policy changes it was critical that a key objective and requirement was to first confirm the reliability of atmospheric detection equipment on which to base any such future procedural or policy changes. This study represents a baseline assessment wherein an attempt was made to obtain an up-to-date fingerprint of atmospheric contaminants while, at the same time, assessing the accuracy and reliability of the monitoring instrumentation. The study provides a baseline upon which to conduct a valid review of the maximum permissible concentration (MPC) of substances found in BR 1326 and, to provide guidance for updating the contaminants list and exposure limits (4).

While current information on submariners' exposure to contaminants can assist in accurately determining potential health effects, it can also assist in evaluating any apparent degree of degradation in performance which could adversely affect operational capability. Thus, collection of accurate data of atmospheric conditions provides much needed information for corroborating current policies and procedures and for substantiating recommendations for altering existing SOP's to prevent any potential reduction in operational capability attributable to submariner exposure to contaminants, now and in the future.

Methods

This study was conducted onboard HMCS Okanagan during the period 4-5 August 1998. It was designed to monitor true environmental conditions, while maintaining routine operational procedures and standard policies. These included all practices for air purification and monitoring of contaminants (Oxygen [O_2], Carbon Dioxide [CO_2] and Carbon Monoxide [CO]), as predetermined by Canada's Navy.

Under "patrol conditions", continuous monitoring enabled a reasonable assessment of air purification capabilities (management of O_2 and CO_2); routine housekeeping procedures (cleaning and cooking); lifestyle effects (smoking); and, system effects (engine, compressor and motor). Monitoring continued during the two-hour snort period to determine the effectiveness of snorting; the resulting air exchange; and, the effects of battery charging. Compounds selected for measurement were those which are potentially life-threatening or carry a risk of producing long-term chronic symptoms. With one exception (particulates) all compounds are documented in BR1326, and thus it was possible to assess compliance with the Standard.

Representative sampling of all air constituents and contaminants were taken in areas where contaminants were likely to be produced or to where they could spread. Air constituents and airborne respirable particulates were continuously monitored, and for those constituents serially collected on adsorption tubes, timings were based upon expected concentrations. Grab samples and colorimetric tube measurements were taken at timings to provide representative concentrations under worse case conditions. All instruments were calibrated minimally pre- and post-sample collection. Body burden accumulation of CO was measured non-invasively from representative volunteer crewmembers (10 smokers and 10 non-smokers) to determine Carboxyhemoglobin (COHb) levels using the formula: COHb %= 0.16 X CO ppm.

All collected data was reviewed, adjusted for baseline variations, collated and plotted. To determine overall exposure to specific air constituents for the continuous real time data, the "area under the curve" was computed for each area over the period monitored.

Results and Discussion

Although the total dive period was 21 hours and 48 minutes, this study was performed in conjunction with dive training exercises. Thus, data collection under "patrol conditions" was not initiated until all training exercises that could artificially alter the submarine environment were completed and the air throughout the submarine was replenished through snorting.

Baseline values for initial CO_2 and O_2 concentrations seemed well outside the normal range of ambient air (O_2, 20.9%, CO_2 0.04%). However, as data collection was initiated 4 hours and 45 minutes after the dive commenced, values are reflective of the O_2 consumption and CO_2 accumulation from crew respiration during initial submergence. It is interesting that with two clearance snorts prior to the start of air monitoring (25 minutes and 1 hour, 1.5 hours apart) the submarine atmosphere was not completely cleared to ambient conditions. The Standard, BR 1326, has indicated that a 35-minute snort will effectively clear the submarine atmosphere. Clearly, on this trial, that was not the case. This suggests that further examination of the effectiveness of snorting to clear the atmosphere is necessary.

During the initial six hours of the dive, the CO_2 levels increased gradually and equally in all four monitored areas. At 0200 hours a sudden increase was seen in CO_2 levels. This is an anomaly associated with instrument re-calibration which was necessitated by temperature and humidity interference with the electronic measuring equipment (3, 5). The real-time and continuous collection of data enabled the anomaly to be corrected for and thus it was possible to analyze the increases of CO_2 over time, and to assess the impact of air purification.

Results indicate that CO_2 canister-activation, in itself, has very little to no effect in reducing CO_2 concentrations in the Control Room and even with continual replacement of canisters, CO_2 concentrations continued to rise in the After Ends and in the Fore Ends. The placement of the absorption devices (fore and aft) and the ineffectiveness of the ventilation system nullify the ability of the CO_2 canisters to reduce CO_2 concentrations, especially while Blackout Curtains are in place. Many contributing factors together account for the ineffectiveness of the absorption units: the configuration of the After Ends; a ventilation supply that does not reach into the living quarters; a poor to non-existent air exchange; canister placement; and, number of occupants in compartments. The bottom line is that purified air is not re-circulated but rather redrawn into the absorption units. However, the open concept in the Fore Ends does allow for a somewhat natural dilution and so, while an actual decrease in CO_2 concentration was not observed there was a slower rise.

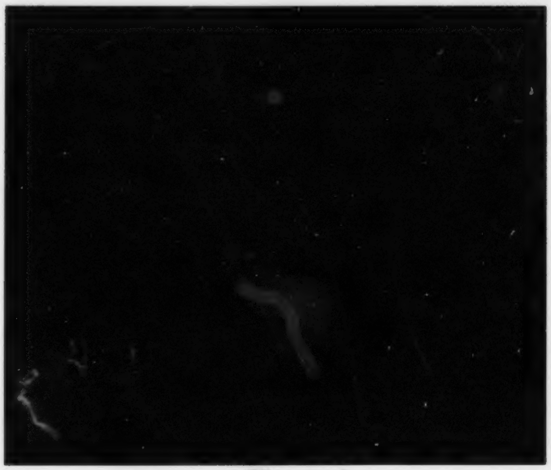

Figure 1.

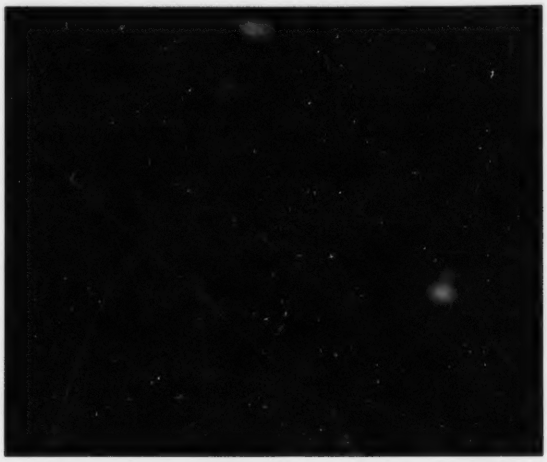

Figure 2.

Figures 1 and 2. Changes in CO_2 and O_2 concentrations and the effects of air purification scrubbing and chlorate candle oxygen generation during patrol state conditions. CO_2 canisters and single chlorate candles were activated simultaneously in both the Fore- and After-Ends. With two CO_2 canisters at 2145 hours and 0150 hours; and four canisters at 0548 hours and 1040hours.

Also as expected, O_2 levels continually declined until O_2 candles were activated fore and aft. The most effective replenishment occurred in the Fore Ends and Accommodation space whereas the effect in the After Ends was slight and in the Control Room, non-existent. This pattern more or less repeated itself after each period of candle activation. Generally, compartments in which the oxygen generators are situated benefited most. Despite candle activation, O_2 levels in the Control Room declined continually, reaching a concentration of 17.9% just prior to snorting. Blackout curtains again appear to curtail any effect which chlorate candles may have in improving O_2 levels. The positioning of the O_2 generators; the configuration of the compartments; the lack of exhaust ventilation and circulation of enriched air; and, the number of crew occupying a space affect chlorate candle effectiveness. Despite all this, O_2 levels did remain within specifications (18-22%) in all areas except the Control Room.

It is interesting that both CO_2 and O_2 levels were kept within specifications although suggestions in the guidelines were not strictly adhered to (1). Carbon Dioxide canisters were activated well *before* the suggested 1% CO_2 concentration was attained (i.e. at 0.5%). There is nothing wrong with this, other than canisters are unnecessarily used to preserve the atmosphere as canister-activation could have been delayed until 10.5 hours into the dive. Alternatively, less rather than more candles were actually used to maintain O_2 levels within specifications (i.e. 8 chlorate candles were consumed vice the 11 to 12 candles which were estimated to be necessary).

While initiation began five hours early, the actual replenishment schedule was every four hours rather than the suggested once per hour; as recommended in the Standard.

It appears that preventative steps can indeed preserve the atmosphere and had the schedule in the Standard been followed, the atmosphere may well have been preserved for a longer period of time. This simply points out that the interpretation and application of the Standard ultimately governs the composition of the atmosphere. The weak link is the interpretation of the Standard and the risk of miscalculation when relying on inaccurate methods of measurement. As early as 1981, it was strongly suggested that the MPC and the calculations governing replacement schedules should be reviewed (6). This has not yet occurred, and with no current guidelines for scheduling or available calculations to predict accurate scheduling, crews must rely on inaccurate measures, past experiences, or memory. Commanding Officers, therefore, are placed in an awkward position of potentially having to allow the atmosphere to rise above specifications in operational situations where they are unable to snort.

Unfortunately, the snort data is not available for those contaminants that were measured by real-time monitoring equipment. Thus, the O_2 values seen after 1000 hours are values estimated from pre-snort grab samples, and have been added to identify the inaccuracy and error of certain detection methods. The current colorimetric method of detecting O_2 is plagued with problems and accurate readings are difficult to obtain at the best of times. Humidity, particulates, and interfering gases all have an adverse effect and when one adds the inherent error of Draeger detection (25%), one can appreciate the magnitude of the problem and the need for reliable, monitoring technology.

The CO concentrations increased progressively during the dive, and can be largely attributable to the smoking policy, which permitted smoking in the galley and just forward of Bulkhead 77. Even though smoking was confined to these areas, no single pocket of CO was detected and the rate of accumulation in each compartment was relatively the same, suggesting CO freely diffused throughout the boat. Cooking fumes also contributed to the CO accumulation but it is impossible to partition out the relative contributions of smoking and cooking.

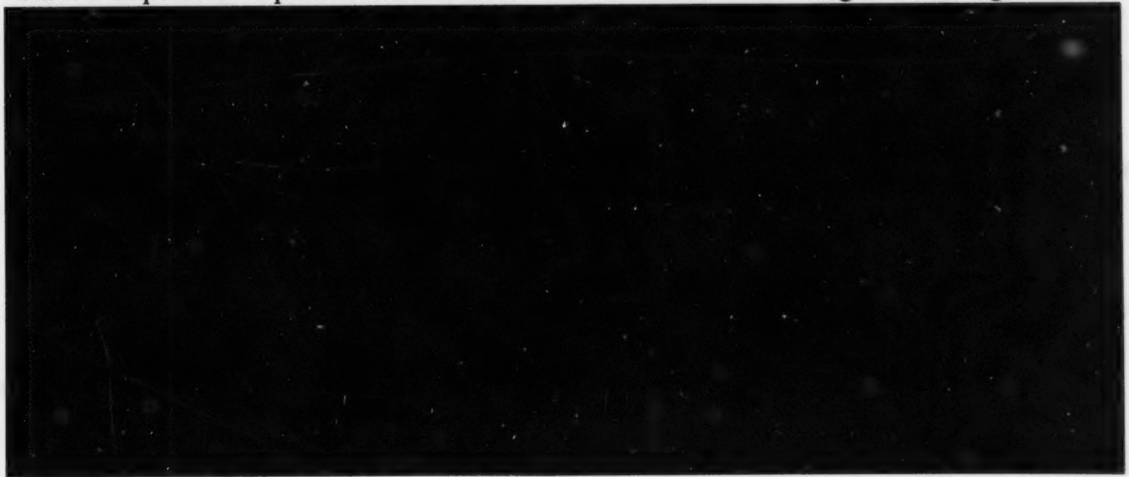

Figure 3. Changes in Carbon Monoxide concentration during Patrol state conditions, together with Carboxyhemoglobin (COHb) concentrations in representative smokers and non-smokers.

There was a sudden 5 ppm increase of CO in the Fore-Ends at 1040 hours; and this is believed to be due to incomplete ignition or incomplete burning of the O_2 candle activated at that time. Previous trials performed on the UK Upholder class submarines have found that O_2 candles can malfunction in just this manner (7). The effect of faulty candles is the release of CO (8). However, a canister for absorbing CO has been designed to operate from the Carbon Dioxide Absorption Unit (CDAU) and results have shown that it is capable of maintaining CO levels within specifications, over a 24-hour period (9).

The biological uptake of CO, COHb, never rose above the Mil. Std. of 10% (10) at any time during monitoring. The average pre-dive COHb in nonsmokers was 0.2%, that in smokers, 2.4%, normal concentrations in such populations. While non-smokers were affected slightly by secondary smoke, the effect was small and disappeared with snorting and with time. Under the conditions studied, there is no indication that the current smoking policy should be altered. This is not to say that a future change in policy may not be necessary. While the intent of this trial was to reproduce a worse-case scenario, the fact remains that worse-case conditions were not attained.

Although Hydrogen is produced under all battery state conditions, monitoring occurred at the "almost full charge state", when maximum off-gassing of Hydrogen was likely to occur (1). The design of the battery ventilation system is such, that battery discharge gases enter the engine compartment and are used by the engines during snorting. This design promotes the risk of battery gases dispersing throughout the boat. For this reason, samples were taken in the Battery Compartment; at the Engine Vent; in the Control Room and in the Accommodation Space. The highest Hydrogen concentration was detected immediately before snort, well within the 2.0% specification for all compartments. While the highest level was detected in the Control Room (0.11%), this concentration did not differ significantly from other compartments. Once the full charge state had been reached, Hydrogen concentrations fell below 0.02% in all compartments. The other products of battery off-gassing (Arsine and Stibene) were not detected in any of the monitored areas.

Figure 4. The total respirable particulates (<10 microns) measured consecutively in the Engine Room, Motor Room, and Control Room. Samples were collected every 10 minutes.

Review of past habitability studies conducted onboard both Canadian Oberons and UK Upholders (1, 5, 7, 8, 9), indicated that no previous analysis had been performed to determine the respirable particulates present in a submarine. Thus, monitoring was conducted consecutively in those areas in which particulates could be present: first in the Engine Room (7 hours); then the Motor Room (3 hours and 48 minutes); and, finally the Control Room (remaining 13 hours).

Since no military guidelines cover the allowable limits for respirable particulates, comparisons can only be made with the civilian industrial standard (11). As crewmembers could move freely between compartments of the submarine, a Time Weighted Average (TWA) exposure was calculated for each compartment. A TWA respirable particulate exposure of 0.677 mg/m^3 was found in the Engine Room; 0.033 mg/m^3 in the Motor Room; and, 0.214 mg/m^3 in the Control Room. The overall TWA exposure was 0.342 mg/m^3 over the entire monitoring period.

The civilian industrial standard is based upon an eight-hour day, 40-hour week. Given the conditions of submarine operations, it would be inappropriate to simply apply it to the submarine environment. Nevertheless, it does provide a convenient yardstick for comparison. The industrial TLV/TWA limit for generic particulates (not specifically classified as silica or asbestos) is 10 mg/m^3 for inhalable particulates i.e. those deposited anywhere in the respiratory tract. As the detector measured quantities less than 10 microns (but could not distinguish size categories below this value), criteria for inhalable particulates were applied in this study. On this basis, the time-weighted concentration of inhalable particulates fell well within the recommended industrial limit. While within the industrial limit, the exposure cannot be considered risk free. This is because the results assume that the particulates are composed of insoluble material, with no known toxicological effect. This may not necessarily be true and further study is required to accurately quantify particulate levels and identify their composition, under a worse case scenario.

Minor contributing contaminants were also monitored to identify potential problem areas and to assess their compliance with the Standard. Ammonia, to determine if gases produced by the sanitary tanks presented a concern; Ozone, if the electrical instruments posed a problem; and, Nitrous gas (NO_x, NO, NO_2) to determine if components of exhaust gases were excessive. All samples were taken by Draeger tube and all results were found to be below the detection limit of the sampling device (Ammonia > 5ppm, Ozone > 0.05 ppm, and Nitrous gas > 0.5 ppm).

Compound Concentration	Accommodation Space mg/m^3	Control Room mg/m^3	Fore-Ends mg/m^3	Engine Room mg/m^3
Benzene	0.176	0.129	0.087	0.249
Toluene	0.535	0.537	0.562	1.145
Ethylbenzene	0.191	0.165	0.068	0.158
m/p-Xylene	0.881	0.729	0.282	0.782
o-Xylene	0.359	0.305	0.122	0.282

Table 1. Total accumulation of primary diesel effluents found in the Accommodation Space, Control Room, Fore Ends, and Engine Room during 20 hours under Patrol state conditions.

With no capacity to cleanse the air while dived, there is the potential that any chemicals brought into the submarine, and/or any chemicals inherent to the submarine, could off-gas and accumulate within the submarine. Table 1 shows the cumulative concentration of all diesel components over the 20-hour observance period, with the highest levels observed in the Engine Room and in the Galley. Excluding benzene, which is found almost exclusively in fuel, the other three compounds are heavily used as solvents (12). Their presence in areas of the boat where fuel is not combusted could be the result of simple dilution throughout the boat and/or the use of cleaning solvents and degreasers within the boat. This was confirmed by Mass Spectrometry where almost all of the volatile organic compounds were found to be diesel fuel aliphatic hydrocarbons or fractions from petroleum products used as fuels, solvents and cleaners (13,14). Even though all compounds were found to be well below specifications, exposure to aromatic hydrocarbons is always a cause for concern. Whether irritants or carcinogenic, they present health hazards to the crew. For this reason, it is essential that some method of identifying their presence be introduced to any submarine-monitoring program.

Conclusions and Recommendations

Although atmospheric conditions were generally found to be within specifications, to successfully manage submarine air quality, ensure the health and safety of the crew and to support efficient submarine operations, we must go beyond simple compliance with regulations. Continued research is necessary to enlighten everyone involved; to guide the development of submarine atmospheric policies and procedures; to define future instrument requirements and selection; and, to validate the feasibility of introducing engineering controls for improving the submarine atmosphere. As a first step, we recommend a review of CO_2 canister replacement schedules, and the rationale behind them. We also recommend that a toxicological review of all items intended for use onboard a submarine be carried out before any items are purchased and that a record of all materials be maintained in a materials toxicity guide.

Any means possible should be taken to reduce contaminant exposures to within acceptable and achievable limits. To determine what is acceptable and what is achievable will require further research and any determination of acceptability must take into account the operational priorities of the submarine. Nevertheless, under 'normal' submarine conditions, it should be possible to make the environment as safe as possible. To do this responsibly, and in an informed manner, will require an objective review and update of exposure limits to all possible contaminants with due regard to risk of exposure; exposure times; toxicity (acute and chronic), biological half-life; and, additive or synergistic effects of other contaminants.

We believe that collaborative efforts between all nations operating conventional submarines can go a long way in solving problems of submarine habitability and ensuring the health and safety of submariners. Such collaboration can reduce or eliminate unnecessary efforts; reveal previous inefficiencies; and, lead to policy and procedural recommendations and implementations of mutual benefit to all nations. Bringing together experienced submarine commanders to share their collective experience in both interpreting and applying a new standard and guidelines for Canada, and expanding that experience and knowledge within NATO, would strengthen our collective capability and enhance our chances for improving the health and safety of submariners.

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REAL TIME AND RETROSPECTIVE SAMPLING ABOARD US NAVY SUBMARINES

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ABSTRACT

Chlorofluorocarbons (CFCs) are currently being replaced with hydrofluorocarbons (HFCs) in US Navy ships. Submarines represent a unique enclosed environment, and the conversion to HFCs has required adjustments in the operation of atmosphere control equipment. In turn, this has necessitated a more complete evaluation of the levels of trace constituents aboard US Navy submarines, in part to ensure that operational modifications would cause no significant changes in the composition of the submarine atmosphere. Previous studies of trace constituent levels aboard Navy submarines have been limited. Volatile organic compounds characterized on several classes of submarines in the late 1980s and early 1990s. More extensive short term and patrol length evaluations were undertaken in from 1993-1998 aboard two classes of submarines. The data from these more recent studies are compared with that from the older studies. In general, most trace constituents measured in these studies were present at low part-per-billion levels, and have been relatively unaffected by changes in operation of atmosphere control equipment.

INTRODUCTION

The global control of Freon 12 (CF_2Cl_2) production has required the use of a hydrofluorocarbon replacement, HFC-134a (CF_3CH_2F), in Navy air conditioning and refrigeration systems. In addition to the required changes in cooling and refrigeration plant operation, which affects all ships, CFC replacement presents a special concern for Navy submarines. The operation of the catalytic CO-H_2 burner was optimized so that CFCs pass without significant decomposition. This is important because CFCs are always present in submarine atmospheres at low part-per-million levels due to small leaks in refrigeration systems; decomposition of CFCs in the burner leads to formation of HF and subsequent deactivation of the catalyst. Replacement HFCs, being more reactive, decompose in the catalytic burner at normal operating temperature (600 °F, 315°C), potentially affecting the long-term catalyst stability. Catalyst deactivation negatively affects CO, H_2 and trace organic constituent levels. Laboratory research has established that lowering the operating temperature of the catalytic burner to 500 °F (260 °C) reduces the decomposition of HFCs to acceptable levels, without significantly changing the CO and H_2 removal rates. However, hydrocarbon decomposition rates also decrease, raising concerns about the effect of changing the burner temperature on trace atmosphere constituent levels. Although additional laboratory studies showed that the buildup of significant concentrations of trace constituents was unlikely, the submarine represents an enclosed environment in which sailors work and live 24 hours a day. Therefore, it was important to have a shipboard assessment of the potential impact of lowering the burner temperature. There was not a significant amount of information about trace organic compound levels aboard submarines, and trace levels could not be readily measured by the on-board atmosphere analysis system. Consequently, a series of shipboard measurements were undertaken.

Atmosphere analysis studies were conducted to characterize the effect of lowering the burner operating temperature on the trace constituent load. Some baseline information existed from studies undertaken aboard several classes of submarines in the late 1980s. These studies consisted mainly of sampling with adsorbent tubes and were targeted at volatile organic compounds such as benzene, toluene and xylene. As discussed below, these studies showed that there were class-dependent variations in constituent levels that were large enough to suggest that measurements made during the CFC/HFC trials ought to be conducted on more than one type of submarine. These preliminary studies also indicated that while there were variations in average concentrations from one location to another aboard any given submarine, these variations were not extremely different from the average levels. Ultimately, evaluations of the trace constituent levels were made during several short (3-5 day) trials using a portable gas chromatograph, canister and adsorbent tube sampling. These results established the conditions under which longer, patrol length studies were undertaken using canister, adsorbent tube and reactive tube sampling. The results of these studies indicated that the alteration of burner operating conditions has had no substantive effect on the levels of trace compounds; moreover, these efforts have further broadened the data base from which longer term, more extensive evaluations of submarine atmospheres are being undertaken.

METHODS

The aforementioned shipboard studies have been conducted with both real-time and retrospective monitoring. Real-time monitoring was conducted using the CAMS (Central Atmosphere Monitoring System), which will not be discussed here. Since CAMS is not designed to obtained trace contaminant data, a few real-time constituent measurements were obtained using portable gas chromatography. In addition, a variety of retrospective analysis tools were used in these studies. Each method involved collection of air samples on board submarines by personnel from NRL or by the submarine crew. Samples were then returned to the laboratory for analysis.

Portable Gas Chromatography: Near real-time shipboard analysis was performed with a HNU Model GC-311 portable gas chromatograph with a photoionization detector. Each analysis required ten minutes with a detection limit for aromatic hydrocarbons was about 10 ppb.
Whole air (canister) Sampling: Whole air grab samples were obtained in SUMMA polished or SilcoSteel (Restek, Inc.) coated sampling canisters having volumes of 1.0, 1.8 or 6 liters. Each canister was appropriately cleaned and tested prior to sample collection, followed by evacuation to 10^{-4} torr for shipping. Grab samples were taken by inserting the bulb inlet in the gas stream of interest and opening the sampling valve. When the bulbs were returned to the lab they were pressurized to a measured pressure (typically 1520 torr) with humidified zero grade air and stored at room temperature until analysis.
Adsorbent Tube Sampling: Initial studies were primarily conducted with Tenax sampling tubes and later studies mainly with Carbotrap 300 sample tubes (Supelco). The latter consist of three types of media (a molecular sieve and two types of activated carbon) combined in a single tube. We have found that Carbotrap tubes have lower backgrounds and longer storage times than Tenax tubes. All tubes were conditioned prior to use and selected tubes were randomly tested. Septum-sealed TDS-300 sample containers (Supelco) were used for storage before and after sample acquisition. Blank levels were typically less than 1 ppb, assuming a one-liter sample volume. In general, 1-1.5 liter samples were obtained over 100 minutes using Gilian Model HFS 113A personal sampling pumps. Flow rates were checked at the beginning and end of the sampling period with Sierra Top Track flow meters. After sample collection, tubes were stored in their septum sealed containers under refrigeration. Aldehyde-ketone sampling was conducted using Waters or Supelco dinitrophenylhydrazine (DNPH) sampling tubes. 40-50 liter samples were collected over a 100-minute period. After sample collection, each sample was sealed in a culture tube and refrigerated.

Analysis of canister and tube samples: Whole air, tenax and carbotrap samples were analyzed by gas chromatography/mass spectrometry on a Finnigan ITS-40 ion trap mass spectrometer system equipped with a Tekmar Aerotrap 6000 thermal desorption/cryogenic trapping and focusing unit. Samples were thermally desorbed from adsorbent tubes onto a cryogenic trap; known volumes of pressurized whole air samples were passed onto the cryogenic trap. After cryo-concentration, the sample was desorbed onto the GC column for GC/MS analysis. In general, calibration standards were generated from certified mixtures (e.g. Supelco TO-14) and permeation tubes (Kintek). Tubes or canister samples and standards were run with co-injected internal standard (e.g. pentafluorobenzene). Response ratios for each compound relative to the internal standard were generated. Once response ratios had been generated over a relevant concentration range, sample tubes were loaded with a known quantity of internal standard and analyzed. Retention times and mass spectra were used to identify the compound of interest. Calibration curves were typically run once a week and check standards were run each day. Agreement between check standards and the calibration curve had to be within 25% or the calibration curve was repeated. Aldehyde/ketone sampling tubes were extracted and analyzed by liquid chromatography on a reverse phase C18 column (25 cm x 2.0 mm) with UV detection at 230 nm. A TO-11 standard (Supleco) was used to generate a calibration curve.

RESULTS

Systematic efforts in the US Navy to quantify trace atmosphere constituents began in the late 1980s. Research scientists from Naval Research Laboratory acquired samples aboard three US Navy submarines in 1987-1988. Samples were collected on tenax adsorbent media and returned to the laboratory for analysis by thermal desorption gas chromatography mass spectrometry. Samples were acquired in duplicate pairs at various locations and times throughout the sampling period (up to one week). The results are summarized in Table 1 as averages for the entire sampling period on each of three submarines.

Table 1. Average Concentrations of Trace Contaminants Aboard Submarines During 1987-1988 Time Period. All concentrations in parts-per-billion (ppb)

Submarine	USS Webster	USS Pargo	USS Alabama
Benzene	14	6	67
Toluene	-	64	101
Xylenes	81	56	41
Ethylbenzene	19	11	8
Octane (C8)	29	15	11
Nonane (C9)	60	29	7
Decane (C10)	66	37	5
Dodecane (C12)	26	19	4
Carbon tetrachloride	-	2	4
Trichloroethane	19	14	163
Trichloroethylene	9	1	29
Tetrachloroethylene	5	0	2
Chlorobenzene	4	3	2

The results from these early studies indicated that for selected compounds of interest, no single trace constituent approached concentrations that were of concern. For example, the Navy established 90-day limit is 1 ppm for benzene, for 20 ppm for toluene, and is 2.5 ppm for 1,1,1-trichloroethane. Typical concentrations in table 1 are 1-2 orders of magnitude lower than these limits. The data also revealed some differences in the trace constituent profiles in different submarine classes. For example, the levels of aromatic compounds and 1,1,1-trichloroethane were higher on the USS Alabama (an Ohio class submarine) than the other two submarines, while aliphatic hydrocarbon levels tended to be considerably lower. The data set was limited, but these trends have been observed in more recent studies, as noted below. Although not shown here, data also indicated that the average level of constituents, as reflected in fan room air, is a reasonable approximation of samples taken throughout the submarine.

Shipboard Studies, 1993-1995. Extensive sampling and analysis of submarine atmospheres was conducted in conjunction with tests on reducing the operating temperature of the CO-H_2 burner temperature. One element of these studies involved short (3-5 day) trials in which real-time and retrospective samples of the atmosphere were obtained during various phases of ship's operations, and during the course of variations in burner temperature. Samples were acquired from an air stream coming directly from the fan room; therefore, samples reflected a well-mixed average of the entire submarine. One outcome of these initial short duration studies was the observation that relatively significant changes in trace constituent levels can occur due to temporary variations in ship's operations. This is shown in figure 1, wherein gas chromatograms obtained at times only four hours apart showed significant changes in trace constituent levels. These changes were also observed in corresponding retrospective measurements and were directly correlated to changes in ship's operations. The results of the short-term studies showed that variations in trace contaminant levels due to variations in ship's operations (ventilation, flank speed) were far greater than changes caused when the burner temperature was temporarily lowered. These studies also pointed out that if sampling was to be undertaken over longer duration periods, it would be necessary to acquire samples in such a way that short term variations were averaged out, otherwise any long term changes would be masked.

Figure 1. Gas chromatograms obtained from air samples acquired during 5-day burner test aboard USS Kentucky, 1994. Chromatograms shown were obtained 4 hours apart.

Patrol Length Studies, 1996-1998. The results obtained from the short-term shipboard studies were followed by patrol length studies in which the ships' force acquired samples at daily intervals over the course of a full patrol. 3 patrols on USS Kentucky and 1 patrol on

USS Boise were followed. On each patrol, the CO-H_2 burner was operated at different operating temperatures for extended periods, and the results from retrospective sampling were compared with the burner operating temperature. The results showed that there was no statistical correlation between the operating temperature of the burner and the trace constituent levels aboard either submarine. On the basis of these studies, the decision was made to proceed with conversion of submarines to HFC use, with corresponding operation of the CO-H_2 burner at 265 C. The concentrations for several different compounds, generated by averaging the daily values over the course of each patrol, are shown in table 2. These values will be compared with patrol length studies that are currently being conducted aboard submarines that have undergone conversion to HFCs.

Table 2. Average concentrations (in parts-per-billion, ppb) and 95% confidence intervals for trace constituents measured by carbotrap sampling aboard USS Kentucky and USS Boise over the course of a patrol.

Submarine	USS Kentucky		USS Kentucky		USS Kentucky		USS Boise	
Patrol	1		2		3		1	
Samples	41 Days		27 Days		33 Days		31 Days	
	Ave.	95% Int.	Ave.	95% Int.	Ave.	95% Int.	Ave.	95% Int.
1,1-Dichloroethene	14.8	8.0	10.1	2.3	8.4	3.1	0.2	0.0
Methylene chloride	5.8	2.5	4.9	2.5	2.7	0.7	2.7	0.6
Chloroform	0.4	0.3	0.3	0.0	1.0	0.3	0.3	0.0
1,1,1-Trichloroethane	39.5	13.6	55.2	13.4	43.3	12.1	0.6	0.1
Benzene	5.3	2.0	6.9	3.1	12.4	3.8	1.4	0.3
Trichloroethene	1.3	0.8	1.1	0.2	1.3	0.2	0.2	0.0
Toluene	19.2	7.0	17.6	3.0	27.8	5.3	10.5	2.1
Chlorobenzene	0.5	0.2	0.3	0.1	0.5	0.2	0.2	0.0
m-Xylene&p-Xylene	26.7	11.9	20.1	3.2	30.6	7.8	4.3	0.9
Ethylbenzene	6.7	2.9	8.9	6.7	7.5	1.4	2.7	0.5
Styrene	6.3	2.7	7.2	1.0	6.3	1.2	6.5	2.4
o-Xylene	19.0	8.6	14.3	2.4	20.1	3.9	5.1	1.4
1,2,4-Trimethylbenzene	84.2	35.4	47.1	11.1	96.4	21.9	14.2	9.5
1,3,5-Trimethylbenzene	275.6	89.4	175.6	42.0	433.0	92.3	63.2	50.3
1,4-Dichlorobenzene	2.6	0.9	6.6	3.0	10.3	3.1	7.4	4.9
1,2,4-Trichlorobenzene	2.3	1.3	1.3	0.4	6.5	9.1	1.5	0.6
Hexachloro-1,3-butadiene	1.4	1.0	0.6	0.2	1.0	0.3	0.3	0.0

CONCLUSIONS

The studies described here have allowed the US Navy to change the operating parameters for the CO-H_2 burner in order to accommodate the use of HFCs aboard submarines. The concentrations of trace components are in the low-ppb to mid-ppb range, and are well below the 90-day limits for the compounds in question. These studies form the foundation for more extensive studies currently underway under the auspices of the Submarine Atmosphere Health Assessment Program at the Naval Submarine Medical Research Laboratory.

Air Quality Monitors in RAN Submarines

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Abstract

The monitoring of air quality in submarines is carried out with a variety of gas detectors for selected air contaminants. The Australian Royal Navy Collins class submarines are fitted with 49 gas sensors which are used, at various fixed locations, to monitor hydrogen, oxygen, carbon dioxide, carbon monoxide, chlorine, hydrogen cyanide, hydrogen sulfide, Otto fuel, nitrogen dioxide, R22, Halon, aerosols and volatile organic compounds (VOCs). They are connected to a central computer (Integrated Submarine Control, Monitoring and Management System) which is programmed with calibration factors and alarm levels. Data from the monitors may be displayed in the Control Room and the Propulsion Control Console and down-loaded for analysis. In addition, independent gas monitors are temporarily fitted for validation purposes during trials.

Most of the detectors are commercial products which use technology most appropriate to the target gas. Many of the sensors are electrochemical, others are infrared or catalytic (hydrogen) based. The sensors are continuously evaluated for reliability and are replaced accordingly. In most cases failures are clearly evident from unrealistic readings while in other cases validation is required with independent sensors.

Air quality trials indicated significant variations of diesel vapour concentrations in the engine room and the regular intake of engine exhausts during snorting. As a result aerosol and hydrocarbon monitors have recently been fitted. A monoethanolamine monitor will also be added.

Introduction

Until 1999 the Royal Australian Navy operated two classes of submarines, Oberons and Collins. The Oberon class submarines had been in service since the 1960s and had only rudimentary air purification and air monitoring equipment. Air monitoring was mainly carried out using colorimetric indicator tubes and an infrared type monitor for refrigerant R-12. In more recent years a hand-held electrochemical detector was used for monitoring oxygen, carbon monoxide, hydrogen sulfide and combustibles.

Some modern submarines are fitted with either a central atmosphere monitor such as the USN Central Air Monitoring System (CAMS) which is based on a mass spectrometer with air sampling via tubing to desired locations. Others use individual sensors strategically located throughout the boat and connected electronically to a central computer. The new Collins class submarines are fitted with 49 gas specific detectors throughout the submarine and connected to the central computer referred to as the Integrated Submarine Control, Monitoring and Management System (ISCMMS). They are used to monitor Hydrogen, Oxygen, Carbon Dioxide, Carbon Monoxide, Chlorine, Hydrogen Cyanide, Hydrogen Sulfide, Otto fuel, Nitrogen Dioxide, R22, Halon, aerosols and VOCs. They are located as follows:

CO_2	Electrical Equipment Space
	Control Room
CO	Machine Generator Room
	Control Room
Cl_2	Electrical Equipment Space
	Control Room
Freon	Lower Accommodation Space
	Auxiliary Machine Space 2
	Auxiliary Machine Space 1
Halon	Electrical Equipment Space
	Control Room
HCN	Machine Generator Room
	Tube Space
H_2	Battery Compartment,
	Machine Generator Room
	Auxiliary Machine Space 2
	Auxiliary Machine Space 1
H_2S	Lower Accommodation Space
	Upper Accommodation Space fwd
	Upper Accommodation Space aft
NO_2	Machine Generator Room
	Control Room
O_2	Electrical Equipment Space
	Control Room
VOCs	Engine Room
Aerosols	Engine Room

Currently, an aerosol and hydrocarbon monitors are being installed in the engine room. This has occurred after a number of air quality trials were conducted and deficiencies in the monitoring system were identified. During the trials independent monitors were used together with data from ISCMMS.

Experimental

A self-logging instrument package was installed in the Auxiliary Machine Space 2 (AMS2) immediately aft of the door to the Motor Generator Room (MGR). The instrumentation consisted of (a) an infrared monitor for carbon monoxide, carbon dioxide and refrigerant R-22, (Uras model 10E) (b) an electrochemical hydrogen monitor with a range of 0-5% (Oldham, TX11), (c) an aerosol monitor for the determination of aerosol (particle) mass concentrations of the size range 0.3 µm to 20 µm (Casella Model AMS 950, UK) and another for measuring particle size distribution at 0.5 µm, 0.7 µm, 1 µm, 3 µm, 5 µm and 10 µm (MetOne Model 237, USA) equipped with a laser light source of wavelength 0.95 µm and connected to an IBM compatible portable note book for data logging. Both aerosol instruments were calibrated with dioctyl phthalate in ethanol with 0.3 µm, 3 µm and 10 µm sized aerosols using a syringed pumped vibrating orifice generator (TSI-3450) with a diffusion dryer and aerosol charge neutraliser. Relative humidity and temperature were recorded using the sensors from a humidity and temperature transmitter (Vaisala, Finland, HMD Model 30 UB). Pressure fluctuations were measured with a pressure transmitter (Transinstruments Model 200B, UK). The instruments (with the exception of the MetOne) were interfaced to a data logger with 15 bit resolution (Datataker Model 500, Australia) and programmed in Microsoft Quickbasic, version 4.5. Details of the program have been previously reported [1].

A calibration gas mixture, from a gas cylinder, was automatically introduced to the monitors (a and b) every 6 h as a calibration check during the trial. The photoionisation detectors were calibrated with 1,3-butadiene (100 ppm in air).

Battery operated, portable instruments were also used for the measurement of carbon dioxide distribution (Vaisala, Geotech and PCO2) carbon monoxide (Oldham, model MX21), hydrogen (Oldham,TX12) at concentrations <2400 ppm, and organic vapours (HNU model PI 101 with a 10.2 eV lamp and ToxiRae model PGM-30 photo-ionization detectors). Monoethanolamine (MEA) was measured using a portable Ion Mobility Spectrometer (IMS), (such as the Chemical Agent Monitor, CAM which is also used for monitoring Otto fuel leaks and manufactured by Graseby Dynamics Plc), UK, modified to selectively respond to MEA and ammonia. R-22 could also be detected with this instrument. Aerosol concentrations were monitored with a Dust Trak, TSI model 8520 laser light scattering particle counter for particle sizes 0.1 µm to 20 µm. This instrument was self-logging.

Carbon dioxide (CO_2) levels in the Control Room (CR) and in the Lower Accommodation Space (LAS) of the Forward Compartment were monitored using infrared (IR) detectors (GeoTech and Vaisala respectively). The GeoTech has a self-logging facility and was also used to record O_2 concentrations, temperature and pressure at 15 minute intervals. Prior to placing these monitors in fixed locations, the CO_2 distribution in the Forward Compartment was determined.

Results and Discussions

Carbon Dioxide

Carbon dioxide concentrations were monitored in the Control Room and the Propulsion Control Console using the boat's sensors. These are infrared type with diffusion air sampling. Instruments of this type are generally reliable but require a resolution < 0.1% in order to observe early trends in concentration changes. Figure 1 shows changes in the carbon dioxide concentrations in the control room. The relatively high carbon dioxide concentrations suggest that the carbon dioxide scrubber was operating during this period. With the carbon dioxide removal system operating carbon dioxide concentrations in the Control Room have not exceeded 1%.

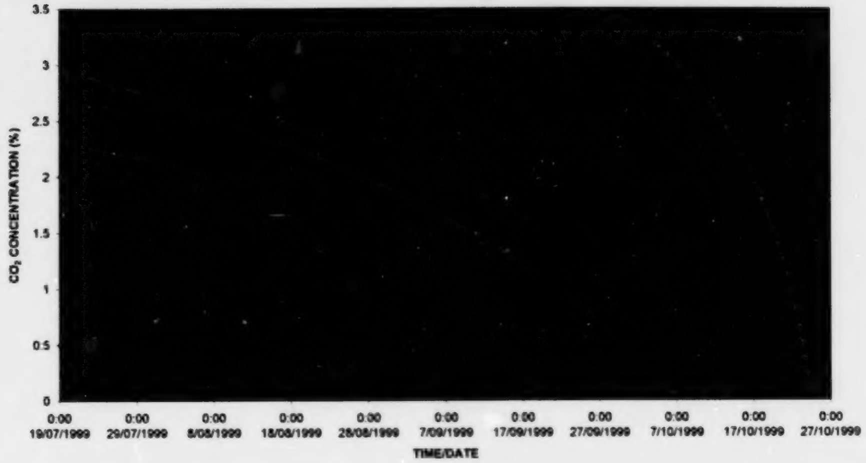

Figure 1. Carbon dioxide levels in the Control Room.

Oxygen

Paramagnetic and electrochemical oxygen sensors are commercially available. The major advantage of the former is its long life compared with the electrochemical sensor which has a limited cell life of approximately 2 years. The disadvantage is its vulnerability to mechanical shock.

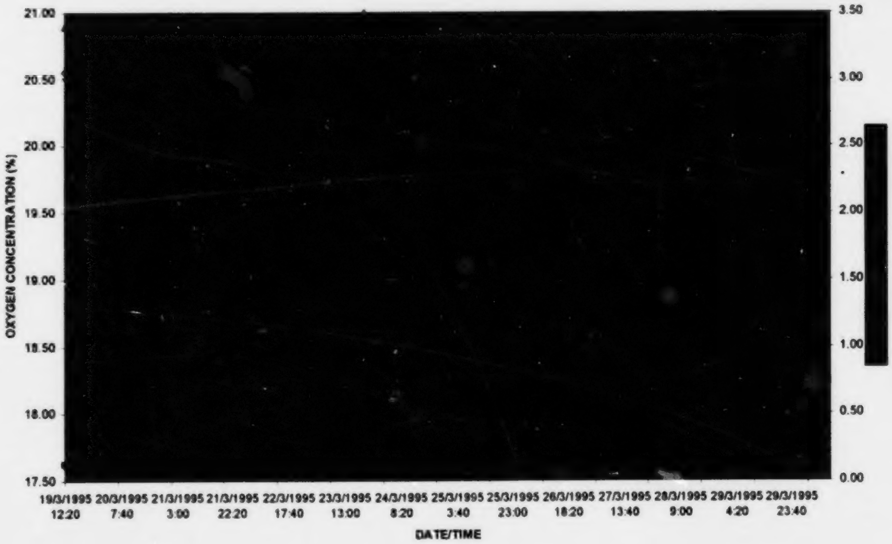

Figure 2. Anti-correlation between carbon dioxide and oxygen with snorting times indicated by pressure changes (upper plot).

The performance of the oxygen and carbon dioxide sensors can be checked against each other as the concentrations of the two gases are interdependent (Figure 2). As with carbon dioxide, the sensor readings can be compared with ambient conditions in order to asses the validity of the data.

Carbon Monoxide

The three types of commercial sensors available for carbon monoxide are photo-acoustic infrared, infrared and electrochemical. Because of interference from hydrogen, electrochemical detectors need to be used with caution. The photo-acoustic detectors, although very sensitive tend to be complicated and hence potentially less reliable. The data in Figure 3 was measured with an infrared detector (Uras, model 10E).There are 2 carbon monoxide monitors, one in the Engine Room and one in the Control Room. As shown in Figure 3, carbon monoxide concentrations are low during snorting (ventilation) and increase shortly after the engines have stopped.

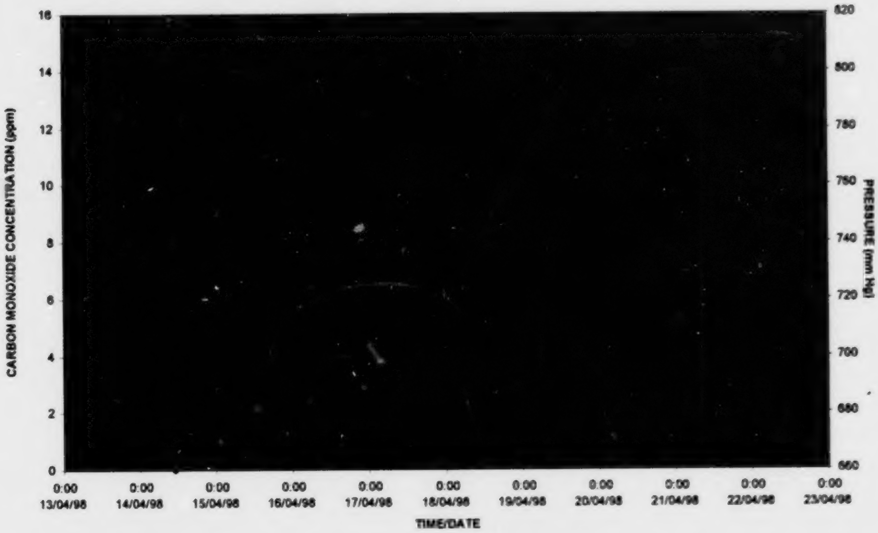

Figure 3. Correlation between carbon monoxide concentrations in the engine room

Hydrogen

The most common hydrogen sensors are electrochemical and catalytic. The Collins class submarines are fitted with several catalytic sensors in the battery compartment. Hydrogen is evolved from the lead acid batteries during charging and the principal method of control is by ventilation during snorting as indicated in Figure 4. An oxidation catalyst is also fitted in the Engine Room for the removal of hydrogen when the boat is dived.

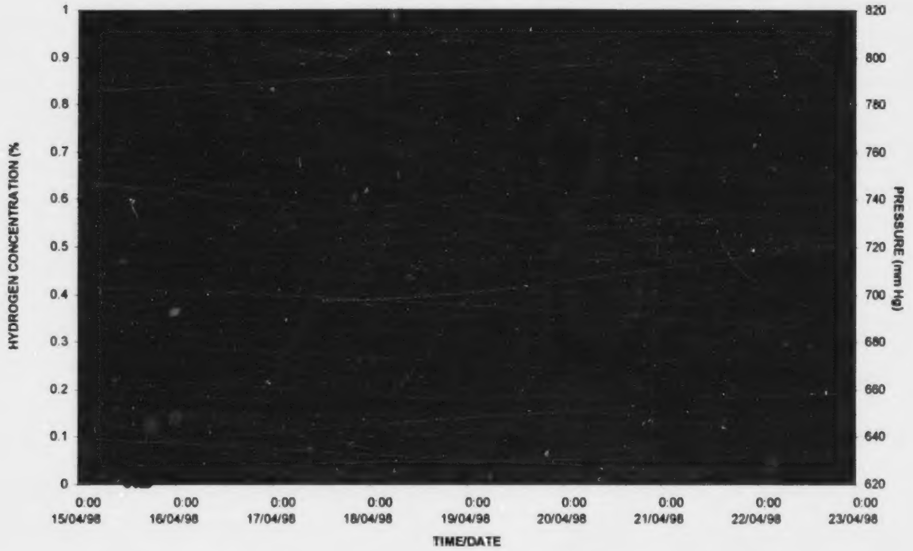

Figure 4. Variation of hydrogen concentration in the Engine Room.

Refrigerants and Halons

These gases are best measured by an infrared type of monitor. Because allowable maximum concentrations are 2000 ppm for short duration exposure the sensitivity of the instrument is unsuitable for measuring background levels which are useful in detecting minor leaks before they cause substantial loss of gas

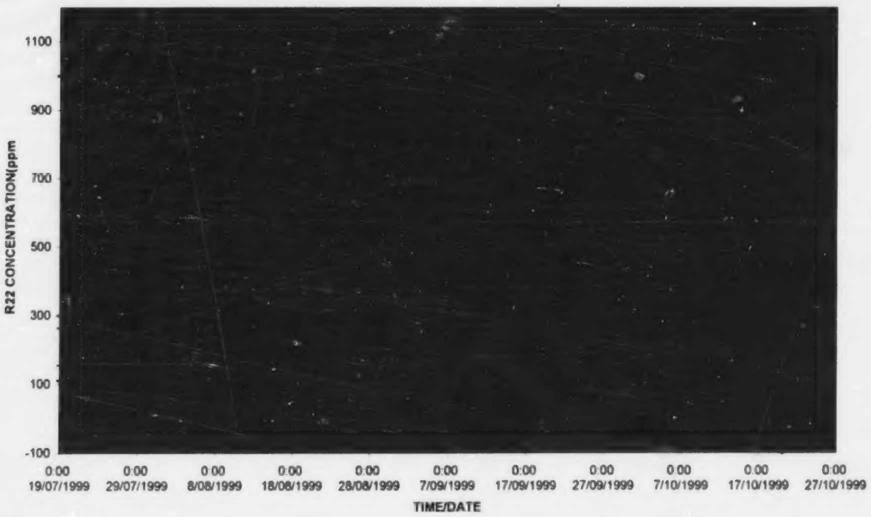

Figure 5. R22 levels measured with the submarine sensor 0-5000ppm range.

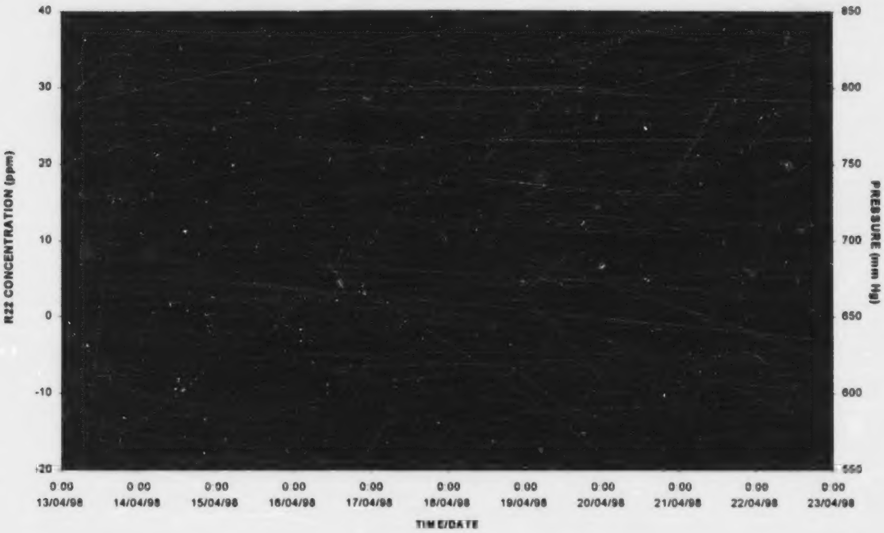

Figure 6. R22 concentrations in the Engine Room

Measurements with a more sensitive instrument (0-200ppm) show insignificant (<10 ppm) concentrations of R22 in terms of toxicity and leaks. A similar result was obtained with halon.

Nitrogen Dioxide

Nitrogen dioxide concentrations in the Engine Room (Figure 7) are still to be validated. However the readings are within a plausible range.

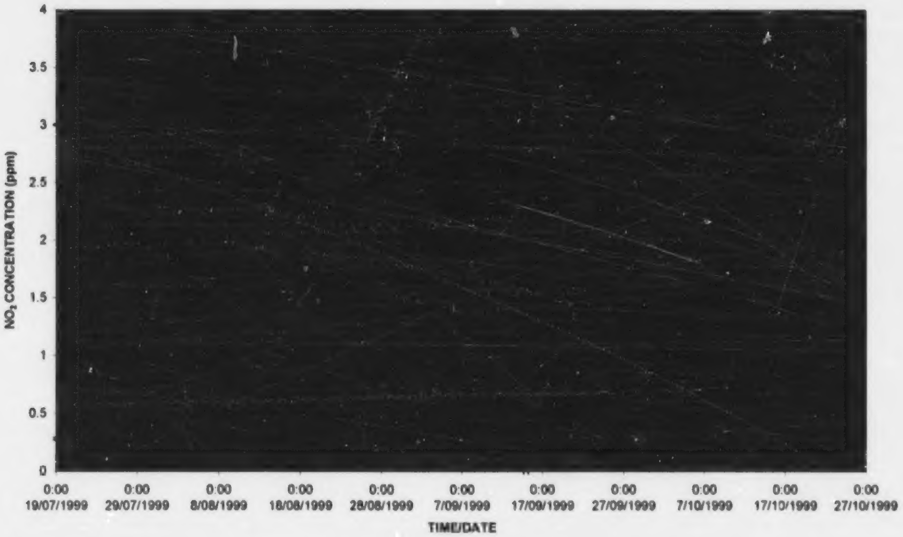

Figure 7. Nitrogen dioxide concentrations measured in the Engine Room.

Chlorine

The primary source of chlorine is likely to be electrolysis of seawater. It is only expected to occur if a substantial amount of water is taken in. The chlorine reading are therefore unexpected and point to a problem in the electrochemical sensor, possibly cross-sensitivity.

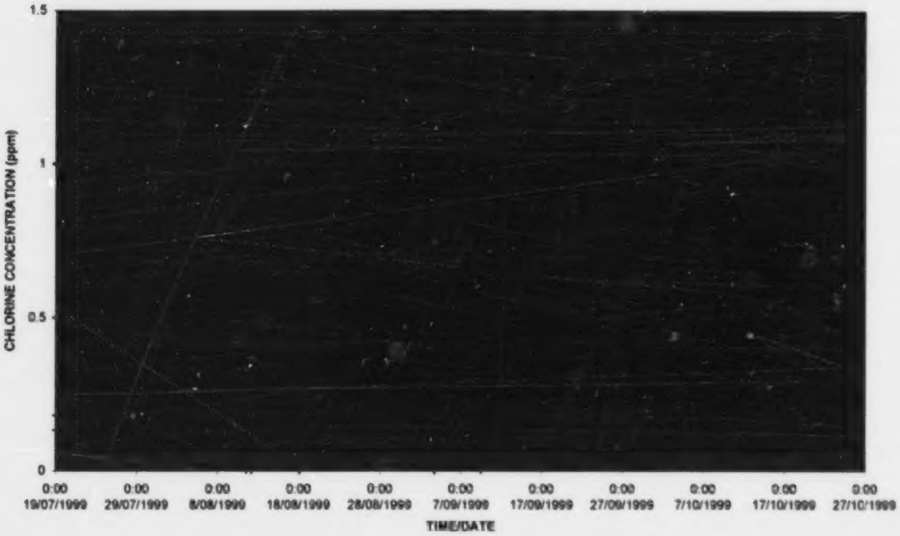

Figure 8. Chlorine readings in the Control Room and Propulsion Control Console.

Hydrogen Cyanide

The purpose of this sensor is to detect hydrogen cyanide as a product of combustion or from the decomposition of Otto fuel. As expected no hydrogen cyanide has been detected over a period of several months.

Hydrogen Sulfide

Hydrogen sulfide may be generated from sewage or oily water wastes within a submarine. It is easily detected at low concentrations (0.1 ppm) by virtue of odour and at high concentrations it is lethal. According to the sensor readings hydrogen concentrations in the UAS, (Upper Accommodation Space) Aft toilets were well above the odour threshold notwithstanding the zero error. The failure of the readings to return to the baseline tends to suggest zero drift error.

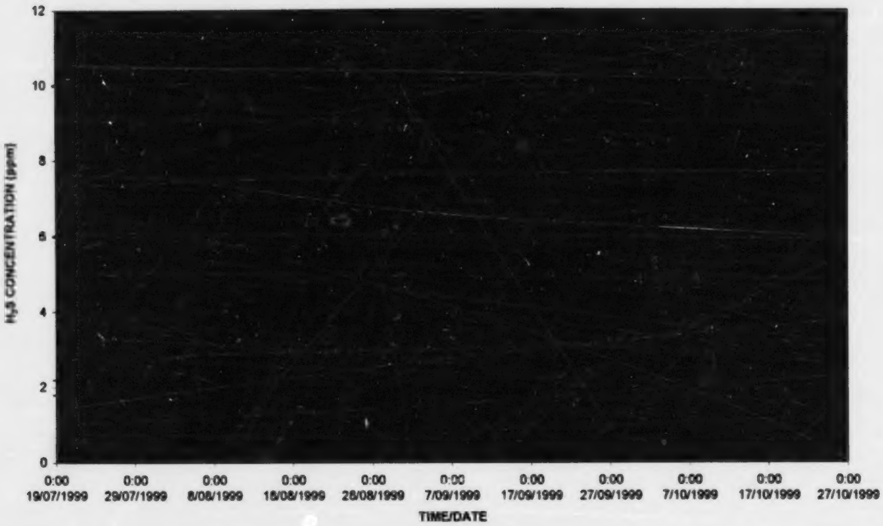

Figure 9. Hydrogen sulfide readings in the toilets

Otto Fuel and MEA(Monoethanolamine)

The only detector that is specific to Otto fuel is the modified Graseby chemical weapons detector, ion mobility spectrometer. This has been found to be troublesome when operated continuously. The cause is believed to be saturation of the molecular sieve drying tube. It has been proposed that an additional electrochemical sensor be used in conjunction with this instrument and that it be activated only when the less specific electrochemical sensor gives a positive reading.

The MEA detector is similar to the Otto fuel monitor with only a minor change to the internal reagent. It is capable of detecting MEA to 50 ppb. The development of the alternative reagent was carried out by DSTO and subsequent development of the modified instrument and calibration was by DERA and Graseby Scientific Plc.

VOCs

One of the major air contaminants in diesel-electric submarines is diesel vapour. Concentrations of 50ppm are relatively common in the Engine Room. Often these concentrations are indicative of fuel leaks or poor fuel management.

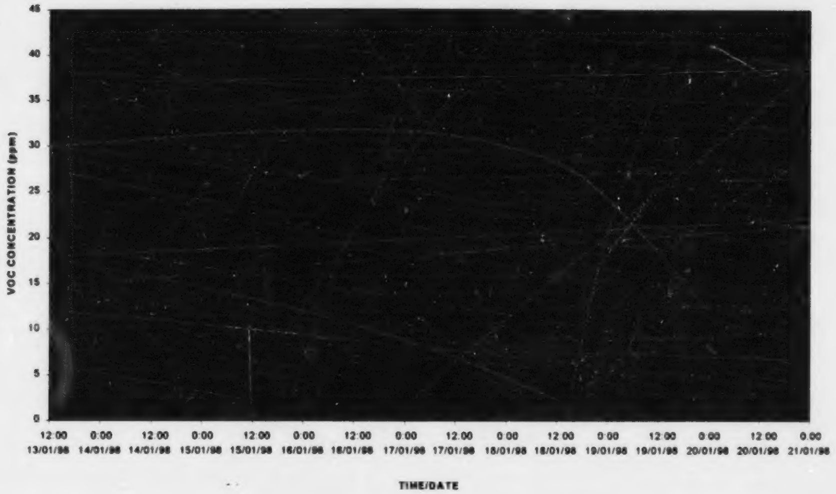

Figure 10. VOC concentrations in the Engine Room under various operational conditions.

Aerosols

The major sources of aerosols in diesel-electric submarines are cigarette smoking and fugitive engine emissions and exhaust intake. As cigarette smoking is not permitted on the Collins class submarines, the diesel engine is the major aerosol source. An aerosol monitor has been recently installed on two of the submarines as a result of a number of trials conducted by DSTO the results of which are presented in another paper.

Conclusions

Commercial gas monitors can be used in submarine applications for the detection of most air contaminants. These can be located near the probable source of the air contaminant and connected to a central computer. However the monitors must be proven to be reliable and their performance needs to be validated against ambient conditions and/or complementary equipment. In some cases where less common contaminants may be present specialised monitors are required.

AEROSOL MEASUREMENTS IN THE ENCLOSED DIESEL ENGINE ENVIRONMENT

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Summary

A limited study of aerosol properties from diesel engines in an enclosed environment was conducted. Aerosol concentrations varied between 0.05 to 12.5 mg/m^3, during the ventilation phase with the engines running to draw in fresh air from a marine environment. Background levels were typically ~ 0.02 mg/m^3, resulting in a continuous averaged concentration of 0.33 mg/m^3, in agreement with mass concentrations determined using teflon, quartz and metricel filter samples.

Particle size distribution measurements suggest mass concentrations are mainly correlated with ~1 μm aerosols. The near identical mass concentration pattern at the fresh air inlet and rear of the engine room suggested the return of diesel exhaust as the prime source of particles.

Chemical speciation studies of metricel filter samples, discount sea salt aerosols as a significant contributor. Analysis of PAHs of one sample, revealed a concentration profile unusually high in 2 and 3-ring PAHs,. with the significant absence of benzo(a)pyrene.

Keywords: Diesel aerosol, size distribution, policyclic aromatic hydrocarbons, benzo[a]pyrene

1. Introduction

Particulate pollution in the open air of major cities, mainly from vehicular emissions, is well known. In comparison, knowledge regarding the exposure to aerosols in the sealed diesel engine environment at isolated marine locations is less recognised. Aerosol production in these situations occur during the ventilation phase, with the diesel engine operating, to draw in fresh air. Various sources include unburnt fuel, steam, soot, combustion products and salt from coastal and maritime environments.

Fine particle pollution from atmospheric aerosols with diameter of less than 2.5 μm is increasingly recognised from epidemiological studies to be associated with adverse health effects (Pope et al 1995). Since the number of ultrafine particles (< 0.1 μm) has a stronger effect than total particulate mass (Oberdorster et al 1995), aerosol size distribution is an important factor in determining the impact of particulate pollution on health (Peters et al 1997). The composition of particulate matter (PM) also contributes to the adverse health effects (WHO 1987). Since incomplete combustion of diesel yields PAHs as by products, there is a need for identification and measurements of their concentrations in the atmosphere.

Thus it was decided to initiate a limited study of aerosol properties from diesel combustion products in confined spaces within the marine environment, including concentrations in air, particle size distribution and chemical speciation analyses of PAHs by HPLC and soluble inorganics by IC.

2. Experimental

Measurements of particulate concentrations at the fresh air intake and rear of the engine room were obtained using two TSI DustTraks (Model 8520), in order to compare their aerosol profiles with time. These instruments rely on light scattering to determine mass concentration. The DustTrak uses a 780 nm wavelength laser diode, with the incident beam perpendicular to the sample flow. The data acquisition rate of particles ranging from 0.1 –20 μm was 1/min, with a time constant of 10 sec. Particle size distributions were not measured in this phase of the study, due to equipment failure. In some cases mass concentrations, varying between 0.1 – 20 μm, in the engine room, were monitored using a Casella AMS 950 sampling at 2.4 l/min. This instrument operated at a wavelength of 950 nm with forward scattering to reduce sensitivity to refractive index, and a time constant of 1 sec. Data was logged every 15 min, using a Data Taker Model 500. Simultaneous measurements of VOC concentrations, using a RAE photoionsation detector, were also logged on the same equipment.

Aerosol size distributions in the size range 0.5 µm, 0.7 µm, 1.0 µm, 3.0 µm, 5.0 µm and 10 µm were determined using a MetOne-237, sampling at 2.8 l/min. Based on light scattering, the sizer operated on a wavelength of 780 nm and was controlled by proprietory software. Logging of particle diameter measurements were coincident with mass concentrations. All aerosol monitors used in this study were calibrated gravimetrically with truck diesel exhaust at concentrations of 12.8 and 18.7 mg/m^3, sampling from a 200 l drum. Filter samples for calibration were collected on Gelman 0.8 µm metricel, sampling at 37 l/min for 10 min, conditioned in a silica gel atmosphere, and weighed at constant mass using a five decimal mass balance. Decaying concentrations with time, and varying between 0.4 - 19 mg/m^3, in the drum were used as an intercomparison for the aerosol monitors. The count rate per 30 sec in the 1 µm size range was used in the intercomparison.

Engine room samples from the fresh air inlet, in the surroundings of a marine environment, were each collected over 24 hr on 37 mm quartz filters for organic carbon analysis by oven baking at CSIRO (Aspendale). Soluble inorganics sampled on the aluminium-backed teflon filters were analysed using IC, also at CSIRO. Prior to analysis, the teflon filters were weighed for total aerosol mass. Quartz filters served as background controls. A metricel filter, also sampled at the air intake in the engine room, was provided for PAH and nitro-PAH analysis by HPLC using UV and fluorescence spectroscopic detection, at Monash University (Churchill Campus). All filter samples were analysed 3 months after collection, due to the remoteness of the sampling site.

3. Results and Discussion

Calibrated and intercomparison truck diesel exhaust aerosol concentrations are shown in Figure 1a, with correlation between 1 µm particles and TSI measured concentrations shown in Figure 1b.

In the marine environment, aerosol concentrations measured at the fresh air inlet and rear of the diesel engine room, are displayed in Figure 2. Large variations in mass concentrations are observed during the ventilation phase, ranging from 0.05 to 12.5 mg/m^3. With the engines turned off, background levels were typically 0.02 mg m^{-3}, resulting in a time averaged value of 0.18 mg m^{-3} at the inlet and 0.33 mg/m^3 at the rear. These averaged values are in good agreement with concentrations of 0.11 - 0.42 mg/m^3 measured on filter samples. These values are equivalent to heavy city traffic of 0.1 - 0.2 mg/m^3, and exceed the ambient outdoor target concentration of 0.05 mg/m^3, as set by EPA Victoria.

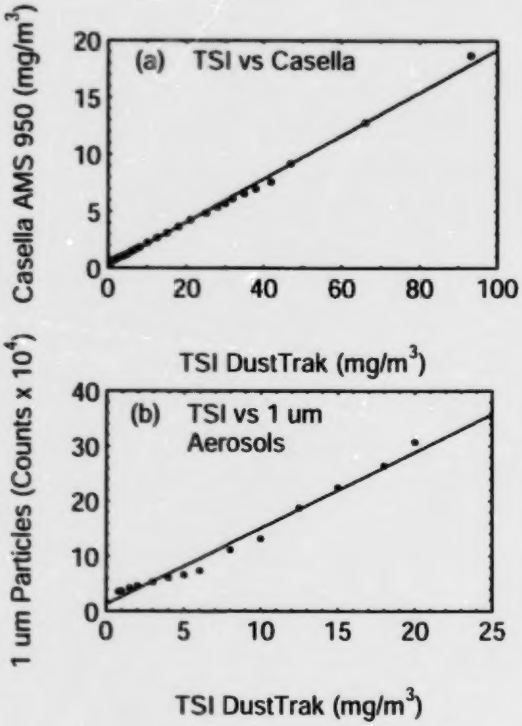

Figure 1. (a) Calibration of TSI mass concentrations using truck diesel exhaust. (b) Correlation of 1 µm particles and TSI measured aerosol levels from truck diesel exhaust.

The coincidence of peak aerosol concentrations between the two locations indicate good mixing conditions of the air in the engine room, as expected from the continuous operation of two large fans blowing from the rear, with face velocities of ~ 30 m/sec. Since averaged aerosol levels in the rear were higher than at the fresh air inlet, this indicates some contribution from fugitive emissions in the engine room. Consequently, the observed large variations also suggest particles being sucked in at the fresh air inlet from an unstable exhaust plume, thus revealing the state of prevailing winds in the open marine environment.

In a separate experiment conducted in a different engine room, mass concentrations varying between 0.01 - 0.15 mg/m^3 were compared with particle size distributions. As is shown in Figure 3, it was found that most of the diesel aerosols were in the 1 - 3 µm size range or less. A similar comparison with particles in the 3 - 5 µm size range did not show agreement with total aerosols. Significantly, the observed aerosol size is less than 2.5 µm in diameter, as these are respirable fine

(PM) and ultrafines, which can be lodged in the pulmonary tissue.

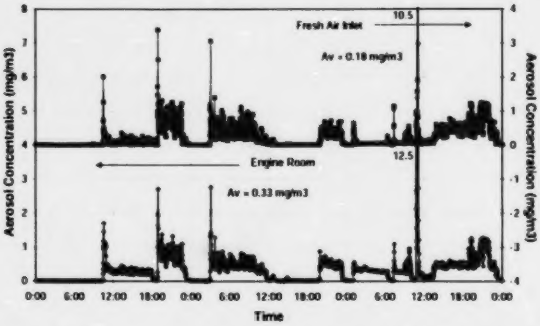

Figure 2. Aerosol Profiles at Fresh Air Inlet and in Engine Room.

It is known from various studies of respiratory symptoms that adverse health effects are associated with particulate mass and number of fine and ultrafine particles (Pope et al 1995). Even though these diesel engine rooms are located in occupational environments, their fairly high concentrations exceeding city pollution levels and the fine particle size warranted further characterisation in terms of the chemical composition.

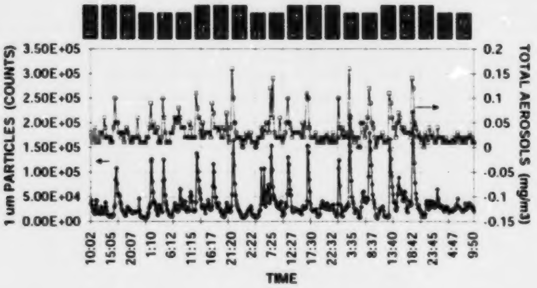

Figure 3. Correlation of 1 μm particles and total aerosol mass.

Chemical speciation studies were conducted for organic carbon content and soluble inorganics, and the analysis results are shown in Tables 1a and 1b respectively. Clearly, the organic component dominates the aerosol mass (50% - 77%), with the inorganics accounting for the balance. Since the particulate matter was observed to originate from the external marine environment during the ventilation phase, it may be postulated that salt spray was the prime source. From Table 1b, the low Na^+, Mg^{2+}, Cl^- and SO_4^{2-}, constituting 23% to 46% of total aerosol mass, provide evidence for discounting sea salt as a major contributor. Although both samples showed Na/Cl ratios greater than that of seawater (Table 2), this can be explained by the possible transport from the large areas of salt deposits along the walls of the air intake, during the ventilation phase.

Table 1a. Summary of components as % of total mass.

Filter Sample	M1	M3
Soluble ions	23%	46%
Total carbon	77%	50%

Table 1b. Concentrations of ionic species on metricel filters M1 and M3 and data quality checks.

Concentration (ng/m3)	M1	M2
H+	6	6
Na^+	818	2840
NH_4^+	128	77
K^+	47	200
Mg^{2+}	50	276
Ca^{2+}	26	159
Cl^-	1328	4110
NO_2^-	11	37
Br^-	8	21
NO_3^-	365	294
SO_4^{2-}	609	2268
$C_2O_4^{2-}$	16	70
PO_4^{3-}	11	27
Acetic	1	1
Formic	22	33
MSA	5	3
F	3	86
total ions	3	11
% of mass	23%	46%
measured conductivity	13.44	35.53
calculated conductivity	13.99	37.48
ion balance	-4.3%	-3.8%

Table 2. Comparison of filter samples M1 and M3 with typical seawater concentrations.

	Seawater	M1	M3
Na/Cl	0.86	0.95	1.07
Mg/Cl	0.20	0.05	0.10

SO_4/Cl	0.21	0.17	0.20
nssNa	0.00	28	38
nssNa/total Na	0.00	49%	19%

Recent studies of truck diesel exhaust sampled directly (Reilly et al 1998) and ambient aerosols in the LA Basin (Venkataraman & Friedlander 1994), suggest a correlation between organic composition of particulate matter and particle size. Real time characterisation of 0.77 – 1.02 μm (aerodynamic diameter) diesel engine smoke particles by laser ablation tandem mass spectrometry indicate an organic composition of predominantly smaller 2 and 3-ring PAHs, including naphthalene (Naph), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phen) and methyl phenanthrenes (Reilly 1998). These PAHs exist mainly in the gas phase under ambient atmospheric conditions (Venkataraman & Friedlander 1994). By comparison, the semi-volatile 4-ring PAHs, including fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA) and chysene (Chr), in ambient aerosols were found in particles of 0.5 – 1.0 μm diameter (Venkataraman & Friedlander 1994). The more volatile species were not analysed in the aerosol samples. Particles of this size were considered to result from the growth of ultrafines directly emitted from vehicles and other combustion sources, by condensation of secondary reaction products on the surfaces. This accumulation mode indicated longer average residence times in the atmosphere. In contrast, the larger and more reactive 5-ring PAHs including benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DbA), benzo(g,h,i)perylene (BgP) and indeno(1,2,3-cd)pyrene (Ind) predominate in the ultrafine ambient particles (0.05 – 0.12 μm). As well, their depleted levels in the accumulation mode particles (0.5 –1.0 μm) formed evidence for aerosol aging (Venkataraman & Friedlander 1994), since the half lives of the 5-ring PAHs range from 1.3 days for BaP to 2.9 days for BbF in particle-free ambient air (Miguel et al 1986).

The HPLC analysis of the composition and concentrations of 20 PAHs commonly found in the environment are shown in Figure4, along with mean concentrations and range found in London (Halsall et al 1994) and Jakarta (Panther & Hooper 1998). Nitro-PAHs were not detected in this sample, which may be indicative of aerosol emissions from a diesel engine in an essentially indoor environment. The PAH profile of submarine diesel exhaust is compared with those of truck diesel and heavy duty truck diesel exhaust are shown in Figure 5. Clearly, the unusually localised and high levels of the 2 and 3-ring PAHs are in agreement with the tandem mass spectral observations, regarding the organic composition of 0.77 – 1.02 μm truck diesel exhaust particles (Reilly et al 1998). In addition, the minor presence of the highly reactive 5-ring PAHs is consistent with their decayed levels found in aged ambient aerosols from the LA Basin (Venkataraman & Friedlander 1994), since the filter samples were analysed by HPLC 3 months after collection. However, most of the carcinogenic 4,5 and 6-ring PAHs (denoted in Figure 4), were found below detectable limits, especially BaP. This suggests that particles from diesel exhaust emissions in this study may possess little or no carcinogenicity.

It has been reported that BaP may indicate stationary sources of PAHs, such as wood burning (Vanderzalm et al 2000), whereas heavy-duty truck diesel exhaust comprised mainly 3-ring PAHs, including methyl and dimethylphenanthrenes and anthracenes (Rogge et al 1993), although BaP contributed about 0.6% of the total PAH profile. Thus the predominant concentration of phenanthrene in our aerosol profile in this limited study suggests low carcinogenic diesel exhaust.

Further, the relatively high concentrations of Naph, Acy and Flu may indicate some presence of unburnt diesel fuel (Reilly et al 1998). The presence of hydrocarbon vapours (up to 30 ppm), in the engine room, lend some support towards this assertion. However, since BaP should be detectable in our filter samples, albeit at low levels, a further and expanded study to include measurements of ultrafine aerosols and vapour/particulate partitioning for assessment of both BaP levels and the fraction of vapour phase PAHs is warranted.

4. Conclusions

This preliminary study regarding the properties of fine (PM) emitted by diesel engines in an enclosed atmosphere, surrounded by a marine environment, indicates that the aerosols of 1 μm in size, may have resulted from condensation of secondary reaction products on primary particles. Contrary to expectations of fugitive emissions from engine leakage or entry of salt spray from the marine environment, the primary source of particles was diesel exhaust return.

The correlation between 1 μm aerodynamic diameter particles and organic composition of mainly vapour phase 2 – 3 ring PAHs with depleted levels of particulate phase, but highly reactive 5 – 6 ring PAHs, was consistent with emissions from heavy-duty diesel trucks. Below detectable concentrations of the most reactive BaP further suggested that the diesel combustion products in this study may have little or no carcinogenicity. Hence, the findings from this limited study indicate that further studies, expanded to include ultrafines and vapour/particulate partitioning of PAHs would be useful.

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Figure 4. Comparison of Polynuclear Aromatic Hydrocarbons (PAHs) in Aerosols from Submarine Diesel Engine (S), Jakarta (J) and London (L)

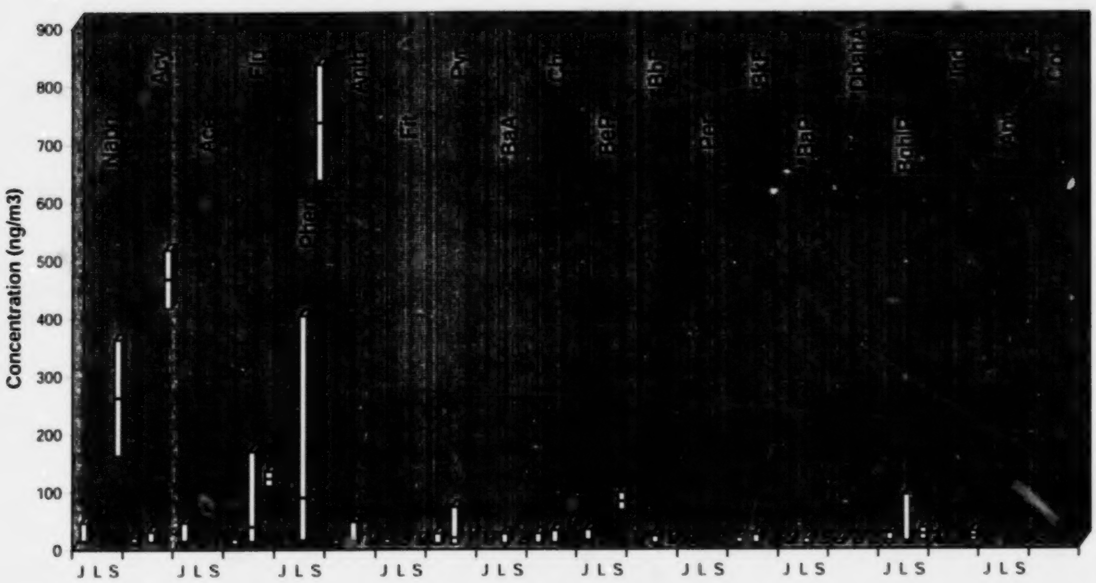
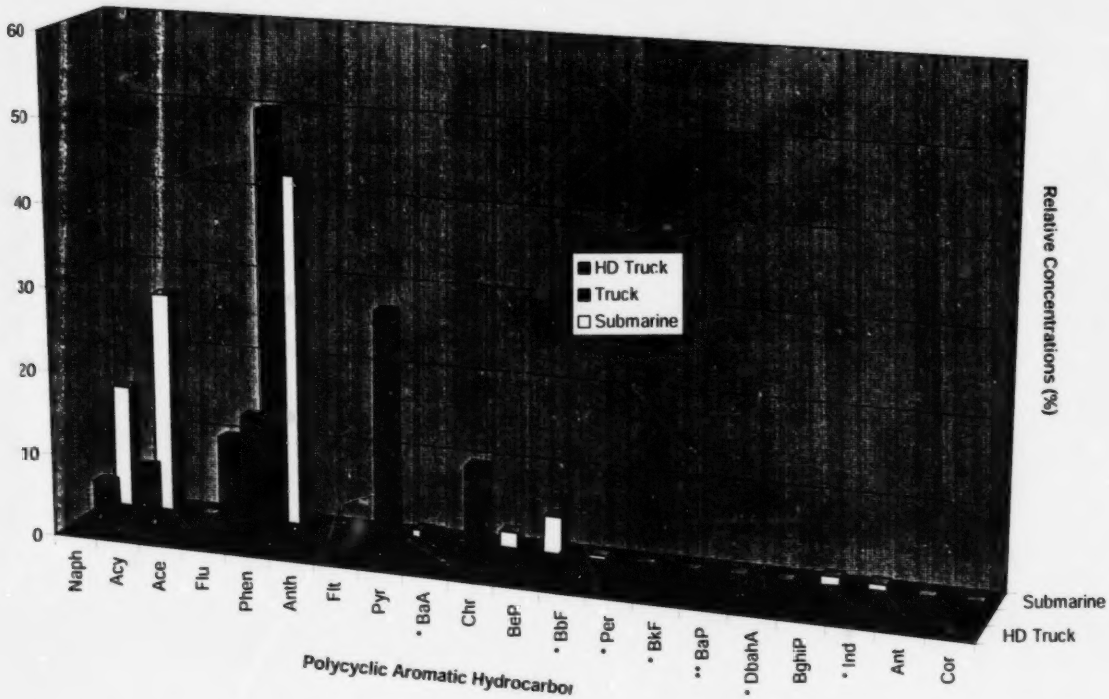


Figure 5. Comparison of PAH Concentrations from Heavy Duty Truck, Truck and Submarine Aerosols.



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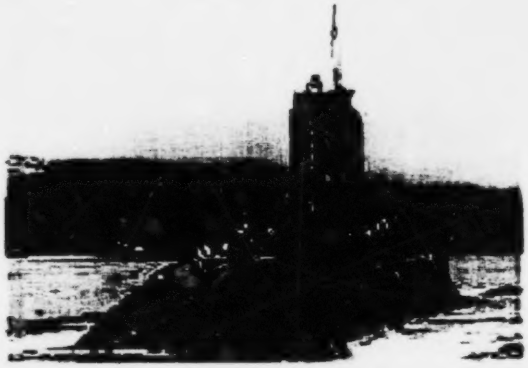

Partie 2

SPASM 2000 - Actes

Troisième Conférence
sur la surveillance et la purification
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W. K. Alexander[1], K. R. Still[1], C. L. Wilson[1], G. B. Briggs[2] . [1] Naval Health Research Center Detachment, Toxicology, WPAFB, OH. [2] Geo-Centers Inc., WPAFB, OH. USA.

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DEVELOPMENT AND USE OF REAL-TIME DETECTORS ABOARD U.S. SPACECRAFT

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Wyle Laboratories, Life Sciences, Systems and Services
and
J. James
NASA/Johnson Space Center

INTRODUCTION

Before 1990, real-time air quality monitoring on U.S. spacecraft had been limited to a few major atmospheric components such as oxygen, carbon dioxide, and water vapor, measured as dew point (1). In response to air quality concerns on Skylab (2), means to acquire real-time data for this unique situation were flown, but ground-based analyses of archival samples remained the primary means for assessing air quality in spacecraft (3, 4). Sensor technology limitations, relatively short missions, and spacecraft resource constraints restricted the use of real-time monitors in the Shuttle program until 1990. A series of Shuttle incidents that degraded the cabin air quality (5) led the National Aeronautics and Space Administration (NASA) to develop the combustion products analyzer (CPA) - the first portable, real-time monitor to routinely fly on Shuttle missions.

The NASA/Mir program was NASA's transition to the space station era with its increase in mission length, more complex spacecraft systems, and greater number of sophisticated payload experiments. Data collected from archival samples during the Shuttle and NASA/Mir programs have been invaluable in identifying compounds to be monitored by real-time monitors on the International Space Station (ISS). Severe air quality degradations (6) caused by leaks and thermodegradations on Mir served to highlight the need for real-time data. In response to heat-exchanger fluid leaks and a major fire, NASA delivered ethylene glycol Drager tubes and the CPA, respectively, to Mir. This equipment was used during all subsequent NASA-Mir missions.

Air quality samples and experience collected on Shuttle and Mir over the last 10 years helped determine how to equip the ISS with real-time air quality instruments. Portable compound specific analyzers (CSA) designed to measure a few compounds in specific situations and a fixed instrument for detecting a minimum of 20 volatile organic compounds (VOCs) comprise the ISS crew health air quality monitors. This array of instrumentation will provide the first comprehensive real-time air quality monitoring available on board a spacecraft for nominal and contingency situations.

COMPOUND SPECIFIC ANALYZERS

The CSA concept, developed by the Toxicology Laboratory, encompasses small, portable monitors that can detect a few compounds that are generally reactive or hard to measure. In response to the pyrolysis of a length of Teflon wire on board the STS-28 mission in 1989, the CPA was the first CSA to be flown on the Shuttle. The function of the CPA was to protect crew health by monitoring key combustion products following a thermodegradation incident in the spacecraft. The CPA sensors detect carbon monoxide (CO), hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen cyanide (HCN). Considering the materials in the spacecraft, these compounds were deemed likely to be the most hazardous ones released in a fire, and the effectiveness of the cleanup could be measured by assessing the rate at which these compounds decrease during decontamination. The crew would remove breathing apparatus when the CPA indicated that the four marker compounds were at acceptable values. The CPA consisted of four electrochemical sensors and a pump configured into a small package, Figure 1.

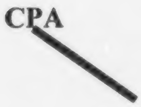

FIGURE 1: Combustion Products Analyzer (CPA) on the Shuttle

Although ground-based testing of the HF sensor was successful, on-orbit results were not reliable. However, the major limitation of the CPA was the CO sensor's cross-sensitivity to hydrogen. Hydrogen is a significant (ppm) air contaminant that accumulates over the course of the mission. This shortcoming required the crew to record daily baseline CO readings that can be subtracted from displayed readings obtained during a fire. This was time consuming for the crew and cast some doubt on the validity of the results. This was apparent following an incident on Mir where the concentration of CO (as indicated by the CPA) reached levels above 400 ppm, which was later verified by analysis of archival samples. The CPA correctly quantitated the CO concentration, but the readings during the incident were considered suspect.

The compound specific analyzer-combustion products (CSA-CP) from Industrial Scientific Corp (Pittsburgh, PA.), Figure 2, addressed the major limitation of the CPA - the CO sensor cross-sensitivity to hydrogen. The CO sensor in the CSA-CP is an electrochemical sensor with a four-electrode design that eliminates the hydrogen cross-sensitivity. Testing has shown accurate CO

TABLE 1: CSA-CP operating range

COMPOUND	Concentration Range
	ppm
Carbon Monoxide	3 - >300
Hydrogen Chloride	0.4 - 30
Hydrogen Cyanide	0.4 - 30
Oxygen	5% - 30%

FIGURE 2: CSA-CP

readings in simulated combustion atmospheres and in hydrogen concentrations exceeding 1000 ppm. In addition to HCl and HCN sensors, the CSA-CP also has an oxygen sensor, which serves as a backup to the primary ISS oxygen monitor. All sensors are electrochemical like the CPA; however, the CSA-CP operates nominally in the passive mode to conserve batteries since it operates continuously as a CO monitor in the ISS. An auxiliary pump and probe are available for active sampling behind equipment racks and other isolated locations. Table 1 shows the operating range for each of the sensors. Currently the CSA-CP is manifested on all Shuttle and ISS missions, but the Shuttle unit is stowed and used only if a contingency event occurs.

In the early 1990's the number of extravehicular activities (EVA) was projected to dramatically increase during ISS construction, and concerns about exposure to toxic propellants led to the development of a hydrazines monitor prototype. Exposure to monomethyl hydrazine, the Shuttle propellant, was possible during EVAs. Additionally, astronauts might be exposed to the ISS propellant, unsymmetrical dimethyl hydrazine, during ISS EVAs. The scenario is that an astronaut returning from an EVA could introduce a small amount of a propellant into the airlock. The reactive nature of these compounds, the low detection limits required (<40ppb), and the constraints of space flight eliminated commercially available detectors. A prototype unit was build from a Graseby Dynamics (Watford, UK) chemical agent monitor (CAM), in which the reactant chemistry was modified for hydrazines detection. The operation is based upon ion mobility spectrometry (IMS) where analytes of interest are ionized and allowed to drift in a weak electric field to a detector. Separation is achieved according to the size and shape of the analyte molecule. The unit, Figure 3, was tested on Shuttle flights STS-37 and STS-49. Results were impressive, particularly the stability of the response (7), but a desire for increased sensitivity and longer periods between instrument refurbishments led to further studies and modifications. Presently, a CSA-Hydrazine, which is a CAMII unit with a modified direct inlet system, is being evaluated for use on ISS and Shuttle.

CSA-Hydrazine

FIGURE 3: Hydrazine monitor being used to check a crewmember for hydrazine contamination following an EVA

A new air quality concern arose during the early missions to ISS – accumulation of CO_2 and other human metabolites when nominal air flow patterns in the Russian functional cargo block (FGB) were interrupted by collapsed air ducts and open panel doors (8). A new CSA, the carbon dioxide monitor (CDM), was one element of the solution to this problem. The CDM was flown for the first time this year and will be permanently manifested on the ISS so that crewmembers working in confined areas can monitor CO_2. The CDM is a commercial unit from Industrial Scientific and the detector is based on infrared spectroscopy. Extensive testing (9) of the CDM, Figure 4, occurred before it was manifested which demonstrated it met all requirements. The CDM can easily meet the linear range requirement of 0.05% to 3.00% CO_2 by volume.

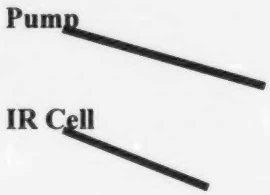

FIGURE 4: ISS Carbon dioxide monitor

VOLATILE ORGANIC ANALYZER

A volatile organic analyzer (VOA) is a complex instrument designed to identify and quantify more than 20 target VOCs in a complex spacecraft atmosphere that may contain 80 or more VOCs. The limited escape options and longer duration missions for ISS have prompted the development of the VOA to protect crew health and safety. The VOA's air quality monitoring role is twofold: 1) routinely monitor the atmosphere for slow accumulation of a contaminant to a level of concern, 2) monitor the effectiveness of decontamination efforts following a contingency such as leaks from a payload experiment or spacecraft system. The most important task for the VOA is to provide data to the crew and ground personnel that verifies that air quality has returned to nominal conditions following a contingency event.

Gas chromatography/ion mobility spectrometry (GC/IMS) was selected as the technology for the ISS VOA. The VOA in Figure 5, build by Graseby, comprises an inlet, two preconcentrators (multisorbent bed), two GC columns, two IMS detectors, and a computer for hardware control and data processing. A prototype VOA risk mitigation experiment (VOA-RME) was flown on the Shuttle (10) to evaluate the operation of the components in a microgravity environment, Figure 6. The VOA-RME results from the flight proved it could perform the analyses in a microgravity environment. An example of results from an air analysis on orbit is presented in Figure 7.

The VOAhas been certified for flight and is being prepared for operation on ISS. The VOA target compounds and its current calibration range are shown in Table 2. Initially, the VOA will analyze the air once per day; however the composition of the air is expected to reach a steady state, at which time the frequency of VOA analysis will be reduced to 1 to 2 times per week. The VOA is designed to operate throughout the cleanup period following a contingency event.

FIGURE 5: ISS VOA positioned in ISS rack Station for a ground based fit check

FIGURE 6: VOA-RME on orbit (STS-89)

VOA-RME

VOA

TABLE 2 ISS VOA target compounds and calibrated range

Compound Name	Concentration (mg/m^3)	Compound Name	Concentration (mg/m^3)
Methanol	0.1-1.5	Ethanol	0.2-3.5
1-butanol	0.3-4.0	2-methyl 2-propanol	0.1-2
Ethanal (qual. only)	0.1-1.2	Benzene	0.1-1.5
m,p xylenes	0.4-5.0	(F22) chlorodifluoromethane	0.3-5.0
o xylene	0.2-2.7	1,1,1, trichloroethane	0.1-1.6
Toluene	0.2-2.6	(F113) 1,1,2-trichloro-1,2,2-trifluoroethane	0.2-2.5
DCM	0.1-1.2	Hexane	0.2-2.4
Propanone	0.1-1.2	Pentane	1.0-12
2-butanone	0.1-1.5	2-methyl, 1,3-butadiene	0.4-5.0
ethyl acetate	0.2-2.4	(halon 1301) trifluorobromomethane	0.1-2.2
2-propanol	0.2-3.2		

FIGURE 6: VOA-RME positive-mode spectrum from STS-89 flight. Siloxanes were not in the identification database, but were identified by analyzing standards.

FUTURE WORK

The Toxicology Laboratory has assembled a group of portable and fixed-position real-time air quality monitors for the first phase of the ISS. These sensors will monitor air contaminants in nominal and contingency situations to protect crew health and safety. The toxicologists and chemists of the Toxicology Laboratory maintain a strong synergism that has been crucial in choosing the correct analytical equipment to provide the data required for assessing spacecraft air quality. In this mode, work has begun on identifying technologies and other real-time monitors that will be needed in the middle phases of ISS and much later as NASA begins to explore the solar system. Already searches have been initiated for CSAs that can measure ammonia and formaldehyde. Studies are being undertaken to assess the levels of ozone on ISS to determine if real-time monitoring is necessary. Obviously, detecting several compounds with one CSA is highly desirable. Finally, a search has started for a second-generation VOA, which is much smaller and less complex than the present VOA, but maintains or improves performance, and is portable. Technologies under consideration include Fourier transform infrared spectroscopy, mass spectrometry, and gas chromatography-ion mobility spectrometry. Further into the future, as NASA sends humans to Mars, resources will drive the search toward micro - and nanotechnologies.

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The Development and Sea Trials of Prototype Fixed-Point and Portable Ion Mobility Spectrometers for Monitoring Monoethanolamine on board Submarines

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ABSTRACT

Monoethanolamine (MEA) is used in equipment installed in submarines for the purpose of removing carbon dioxide (CO_2) from the enclosed atmosphere. A prototype fixed-point continuous monitor for MEA was developed[1] and subjected to laboratory testing. The spectrometer was capable of detecting MEA over a range of temperatures and without interference from other contaminant species normally found in the atmosphere of a submarine, at their respective Maximum Permissible Concentrations (MPCs). Subsequently, the monitor was subjected to sea trials on a submarine. The concentration of MEA was monitored in the CO_2 scrubber compartment over a period of three months and found to be within the MPC for a continuous ninety-day period (MPC_{90}) for the majority of the patrol. The concentration only briefly exceeded the MPC_{90} but did not exceed the MPC_{24} (MPC for a continuous 24-hour period), and was rendered very quickly below the MPC_{90} level. Following the success of the continuous monitor, a prototype portable MEA monitor was developed and also subjected to sea trials in order to investigate the operability of the instrument on board and to determine the atmospheric concentrations of MEA accumulated in various compartments within a submarine. The monitor remained fully functional throughout the trials performed on a submarine, and calibration was stable in excess of eight months spanning the calibration and trials period. The results from the sea trials indicated that the atmospheric MEA vapour was most concentrated in the compartment containing the CO_2 scrubbers. Following ventilation of the submarine, it was found that the MEA concentrations re-established equilibrium over a relatively short period of time, but were maintained within manageable levels.

The development of the monitor has been successful, but further development will be required before the monitor could be accepted into service.

INTRODUCTION

An instrument designed for the continuous fixed-point monitoring of MEA was developed [1], evaluated, calibrated, and subjected to sea trials in the CO_2 scrubber compartment of a submarine. The purpose of the trial was two-fold. It was necessary to determine the atmospheric concentrations of MEA and to prove the functionality of the prototype instrument. As reported previously[1] the monitor was capable of detecting MEA over a range of temperatures and without interference from other contaminant species normally found in the atmosphere of a submarine, at their respective MPC_{90}s. Due to the success of the project, the Ship Support Agency / Marine Auxiliary Environmental and Steam Integrated Project Team MAES5c (SSA/MAES IPT/MAES5c) sponsored the Defence Evaluation and Research Agency (DERA) Bridgwater Laboratories with the development of a prototype portable MEA monitor. The purpose of this project was to evaluate the operation and suitability of the instrument for monitoring on board different classes of submarine, and to determine the concentrations not only in the scrubber compartment but also in as many other compartments as possible.

EXPERIMENTAL

MEA vapour generation and calibration

Vapour generators were set up with permeation sources installed, to deliver a range of concentrations of humidified MEA vapour under conditions of dynamic air flow, samples of which were analysed by ion chromatography. Where appropriate, contaminants were introduced into the system by means of additional permeation sources.

Prototype MEA monitors

The prototype fixed-point MEA monitor was a modified SICS Mk10 (a chemical warfare agent monitor used on surface ships). The prototype portable MEA monitor was a modified CAM™ (the hand-held chemical agent monitor). Modifications to both instruments included replacement of the membrane inlet system to improve the speed of response and recovery, changes to the internal chemistry, and software changes.

Prototype MEA monitor testing

The MEA monitors were connected to a portable computer, programmed with the necessary software to record trials data. The MEA monitors were exposed to the MEA vapour source and the ion mobility spectra recorded throughout the test periods for subsequent analysis.

Pre-trials evaluation

The following characteristics of the fixed-point monitor were evaluated: response and recovery, precision, stability of response, dynamic range, temperature and humidity effects, and interference rejection, tested against possible submarine atmosphere interference species at their maximum permissible concentrations (MPCs).

The portable monitor was evaluated for response and recovery, stability of response, and dynamic range.

Sea trials

Two sets of sea trials have been completed. During the first set the fixed-point monitor and a portable computer were installed inside the scrubber compartment of a submarine. The ion mobility spectrum was recorded continuously for the duration of the operational tour.

The second sea trial was conducted on another class of submarine and aimed to test the effectiveness of a portable monitor and to determine the level of MEA distributed around the submarine. The portable monitor and computer were used to record MEA levels in various compartments throughout an operational tour. The monitor was also used to conduct surveys of the submarine to find the level of MEA in each compartment and to determine the level of homogeneity. All recorded data was subjected to post trials analysis.

Post trials calibration

The calibration of both monitors was checked after the sea trials.

RESULTS

Pre-trials evaluation

The performance characteristics of the fixed-point and portable monitors are summarised in table 1. The times to equilibrium response and recovery were concentration dependent; for example, figure 1 shows the rate of the portable monitor response to MEA as a function of concentration. Figure 2 shows the response curve for the portable MEA monitor over its dynamic range. Figure 3 shows a typical ion mobility spectrum for MEA (RIP is the reactant ion peak formed).

Performance characteristic	Fixed-point monitor	Portable monitor
Response (90%)	90 s	<2.5 min
Recovery (90%)	< 10 min	4 min max.
Precision	<2.5% CV*	-
Stability of response	Stable for > 3 months‡	Stable for 8 months
Dynamic range	<0.1 to 2.5 ppm_v	0.05 to 3 ppm_v
Temperature range	15 to 40°C‡	-
Relative humidity	<6% CV @ 6 to 82 %	-
Interference rejection	No interference found at the MPCs	-

*CV = coefficient of variance

‡Tests not conducted outside the stated range/time span

Table 1: Summary of performance characteristics

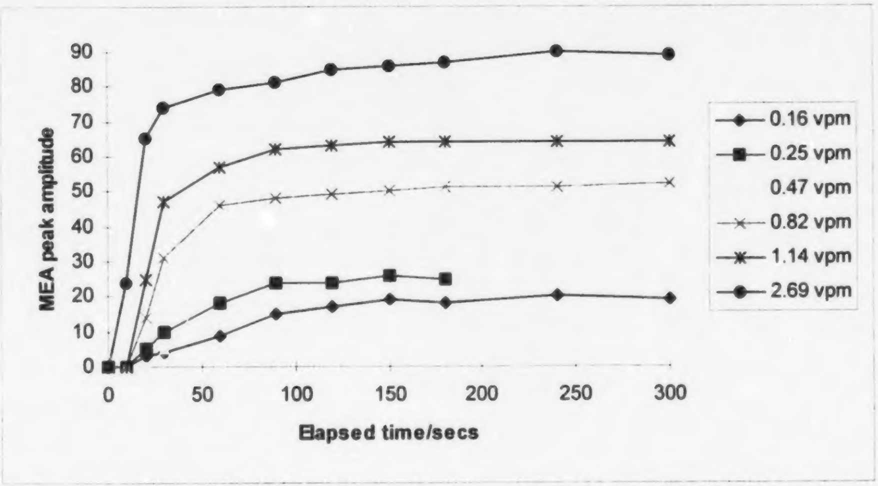

Figure 1: Rate of the portable monitor response to MEA as a function of concentration

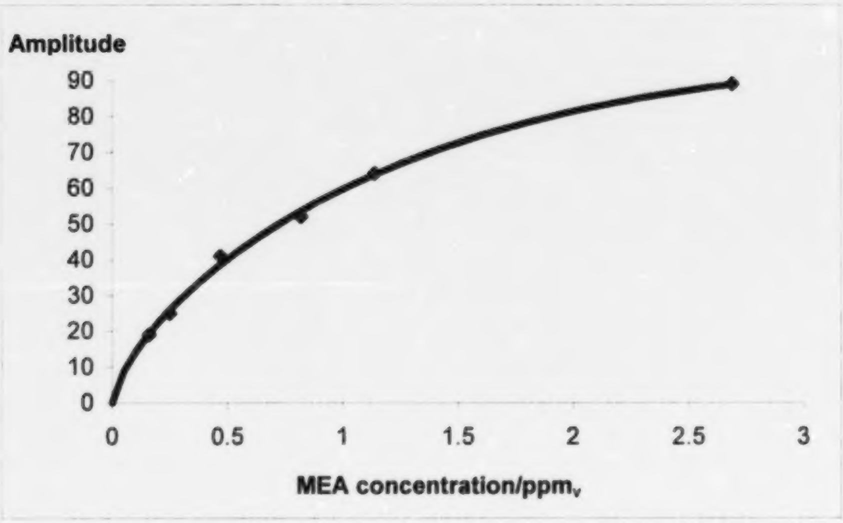

Figure 2: MEA peak amplitude as a function of concentration

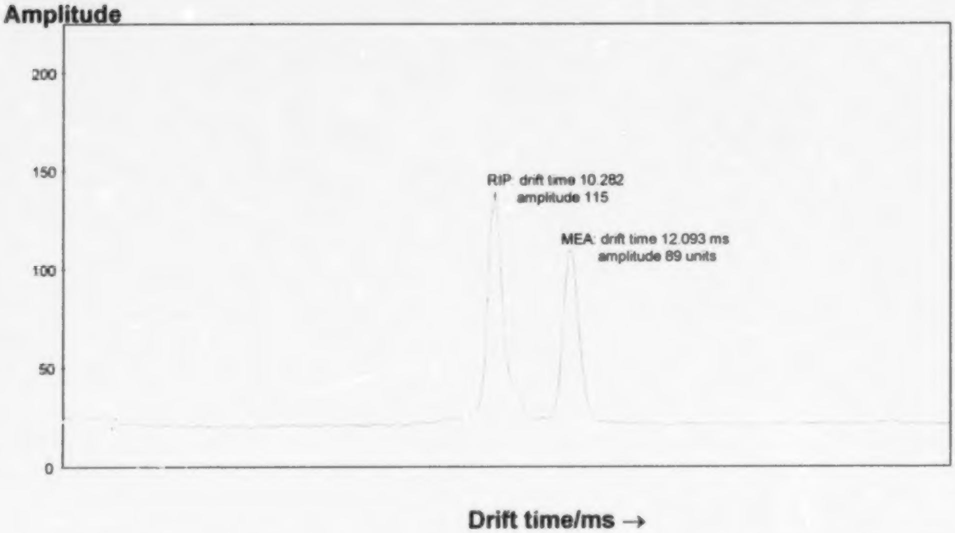

Figure 3: Ion mobility spectrum for equilibrium response to 2.69 vpm MEA

Sea trials

The fixed-point monitor recorded that MEA vapour was always present within the scrubber compartment but only briefly exceeded the MPC_{90} (MPC for a continuous 90 day period).

The portable monitor trials showed that the range of MEA concentrations was approximately 0.05 to 2.5 vpm, the highest MEA concentrations being recorded in the compartment housing the CO_2 scrubbers. In the forward section of the submarine the levels of MEA vapour decreased with distance from the scrubber compartment; in the aft section of the submarine the MEA concentration was homogeneous. Again, only MEA concentrations within the scrubber exceeded the MPC_{90}. Following ventilation of the submarine, it was found that the MEA concentrations re-established equilibrium over a relatively short period, but were maintained within manageable levels.

Post trials calibration check

The calibration checks of the monitors after completion of the trials indicated that the calibrations were stable for several months.

DISCUSSION

The continuous MEA monitor was successful for the fixed-point determination of the MEA vapour profile in the scrubber compartment. The instrument weighs approximately 17 kg (an additional 8 kg for the shock mountings and carrying brackets) and has dimensions of 284 (400) x 216 (270) x 560 mm (the numbers in brackets including the shock mountings).

The portable MEA Monitor was designed to determine the concentration of MEA vapour in various compartments and ideally suited for use in submarine environments. It is a convenient, easy to use, hand-held instrument appropriate to submarine operational requirements. The instruments dimensions are 390 mm x 145 mm x 80 mm, and it weighs approximately 2.5 kg, including a 6V Ni/Cd rechargeable battery. The MEA monitor incorporates the widely proven detection system from the original CAM, with enhanced sampling and detection systems, which provide improved response and recovery characteristics and greater interference rejection. The replacement of the membrane, which requires heating, with a capillary inlet results in less power being drained from the battery, thus extending battery life compared with CAM. The life of the battery under these conditions has not yet been determined. There is an automatic battery check so if the voltage becomes too low a warning symbol is displayed.

The 4-heptanone[2] dopant source was assembled for the trials and performed as expected for eight months, encompassing the trials period. However, calibration following the trials was delayed for three months due to transit problems, at which time it was found that the dopant source was not effective and had to be replaced. Subsequent calibration checks at the MPC_{90} level indicated that the calibration was reproducible. However, in order to introduce the portable monitor into service the development of a long term, stable dopant source may be necessary.

The portable monitor specification drawn from the trials is as follows: limit of detection 0.05 vpm; dynamic range 0.05 – 2.7 vpm; 90 % response < 2 minutes (typical); 90 % recovery < 4 minutes (typical); environmental temperature 0°C to + 40°C operating and -30 °C to +70°C storage.

The response and recovery characteristics emphasise the difficulties of monitoring high surface active materials such as MEA where prolonged exposure to high concentrations results in longer recovery times, and exposure to lower concentrations results in longer initial response times.

The analysis of the trials data showed that in the scrubber compartment the bar responses were always between four and seven bars, out of a possible maximum of eight bars, equivalent to a range of 0.5 vpm to 2.5 vpm. The MEA concentration in one other compartment reached 0.25 vpm on one occasion, but generally only trace levels of MEA vapour, between 0.05 vpm and 0.1 vpm, were detected in the other compartments where MEA vapour was registered. This indicated that MEA vapour spread into other parts of the submarine adjacent to or linked to the scrubber compartment. The results of surveys conducted with the monitor indicate that the level of MEA in the atmosphere falls quickly with distance from the scrubber compartment. Away from compartments immediately adjacent to the scrubber compartment MEA is evenly distributed throughout the submarine and a level of homogeneity is demonstrated.

CONCLUSIONS

The continuous MEA monitor was a successful means of determining the MEA vapour profile in a single compartment of a submarine. The development of the MEA monitor as a convenient, hand-held robust means of detecting MEA vapour in real time was successful for determining MEA in all compartments in a submarine. The monitor was capable of detecting the required dynamic range and had an appropriate limit of detection.

As MEA has been recorded at various concentrations in the submarine atmosphere there is a requirement for risk analysis for localised real-time monitoring of the vapour. It would be advisable to record MEA concentrations in other submarines, for comparison of results.

The Monitor was not only useful for determining MEA concentrations but also the length of time required for MEA concentrations to accumulate.

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CHARACTERIZATION OF AIR QUALITY ABOARD SPACECRAFT USING ARCHIVAL SAMPLERS

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INTRODUCTION

Archival air sampling on spacecraft has been accomplished as an element of crew health and safety measure since the Gemini program (1). Compound concentrations obtained by ground-based analyses of archival samplers are compared with established requirements (Spacecraft Maximum Allowable Concentrations-SMACs) to assess the quality of the air during the mission. The importance of comprehensive, on-orbit archival sampling has grown as spacecraft have become larger, missions longer, and air revitalization systems more complex. Consequently, more archival samplers are manifested on spacecraft such as the International Space Station (ISS) and improved sampling equipment and ground-based analytical methods have expanded the capability of the samplers.

Spacecraft are nearly-closed environments that rely on various means of air revitalization to clean and recirculate the air (2 and 3). The Environmental Control and Life Support System (ECLSS) is designed to maintain a safe balance between generation and removal of air contaminants in nominal conditions. The main sources of air contaminants aboard spacecraft are shown in Figure

FIGURE 1: Typical sources of spacecraft air contaminant

1. The purpose of archival sampling is to verify that the spacecraft air is safe to breathe during the mission, that the ECLSS performed nominally, and to identify contaminants that may have caused any crew symptoms, which might be related to air quality degradation.

During the Shuttle era there have been several in-flight air quality incidents, mainly overheated wiring and leaks of payload chemicals (4). The number and severity of air quality degradations increased for U.S. astronauts staying on the Mir Station during the NASA/Mir program (5). Archival samplers were acquired following the most dramatic of these events on Mir: the fire caused by the solid fuel oxygen generator. Results of the postflight analyses of these samples confirmed the effectiveness of the cleanup and verified that nominal air quality was returned within 36 hours. The complementary nature of archival samplers and real-time monitors was demonstrated by a second incident on Mir in which carbon monoxide (CO) was released. A real-time CO monitor was used to determine CO concentrations during cleanup. Archival samples were taken to verify the CO concentrations reported by the real-time monitor.

SAMPLING ON ORBIT

The Toxicology Laboratory at Johnson Space Center is charged with providing the means to assess the air quality aboard all spacecraft where a U.S. astronaut is present. Toward this end, the Toxicology Laboratory has adopted several commercially available samplers and developed other unique sampling hardware to meet spacecraft requirements. When selecting archival samplers for flight, consideration must be given to minimizing size, weight, power, crew time, and complexity. Currently, 300-mL Summa-treated canisters are used to collect instantaneous grab samples of the air (Figure 2A). The grab sample containers (GCS) provide information on a range of compounds from very volatile (e.g., carbon monoxide) to less volatile compounds (e.g., xylenes). Complimenting the GSC is a device developed at JSC: the solid sorbent air sampler (SSAS). The SSAS (Figure 2B), which is about the size of a 1-lb. coffee can, contains 8 sampling tubes, each containing multiple sorbents for collecting volatile organic compounds. During the mission, the SSAS's sample pump pulls cabin air through a tube for 24 hours, then a valve is manually switched to allow cabin air to flow through the next tube. In this manner, seven time-integrated samples of air can be collected on each mission. Formaldehyde is a very reactive compound that is not effectively sampled by either GSC or SSAS methods. Therefore, a passive formaldehyde sampler (Figure 2C) is used to collect formaldehyde from the spacecraft

A **B** **C**

FIGURE 2: NASA space flight air samplers. A) GSC, B) SSAS, C) Formaldehyde sampler

air. In the course of a typical Shuttle mission one GSC sample is acquired just prior to loading the crew into the spacecraft. This serves as a baseline sample of the cabin atmosphere. Two GSCs are carried into orbit, where one sample is acquired near the end of the mission, and the other GSC is a contingency sampler used if the crew senses an air quality problem. If a Spacelab or Spacehab is flown on a Shuttle mission, then the SSAS and extra GSCs may be manifested. Formaldehyde samplers are now manifested on each Shuttle mission.

The sampling strategy for the permanent-manned presence on ISS is to collect GSC samples once per month and upon first entry to modules added to the stack. The SSAS will acquire samples every two weeks in both the Service and Laboratory modules. Additionally, formaldehyde monitors will be deployed once per month in the same two modules. Extensive sampling of each ISS module is being conducted with GSCs and formaldehyde samplers during Shuttle docking periods. Results of the sampling will establish an air quality baseline prior to arrival of the first permanent crew later this year.

GROUND-BASED ANALYTICAL TECHNIQUES

Once returned to the Toxicology Laboratory, the GSCs undergo several gas chromatographic (GC) analyses using a variety of detectors to quantitate the highly volatile compounds in the air. Carbon monoxide levels are determined by a helium ionization detector; carbon dioxide and hydrogen concentrations are measured by a thermal conductivity detector, and methane and ethylene levels are found by a flame ionization detector. Following these analyses, the GSC samples are then subjected to gas chromatography/mass spectrometry (GC/MS). Although the GC/MS protocol follows the U.S. Environmental Protection Agency's (EPA) TO-14 method, a modification to the target compound list incorporates numerous polar compounds such as acetone and ethanol into the analytical scheme. Ground-based procedures for the SSAS are somewhat unconventional, but have proven to be very successful. Upon return, each tube of the SSAS is thermally desorbed into a 500-mL Summa-treated canister with a flow of nitrogen and then the canister is pressurized to atmospheric conditions. Water is added to the canister before tube desorption to maintain approximately 50% relative humidity. The sample is then analyzed by GC/MS following the modified TO-14 method previously mentioned for the GSCs. Desorbing the SSAS into canisters provides two major advantages: 1) if a GC/MS failure occurs during the run, another aliquot can be run from the canister, and 2) if a particular compound concentration is too high, the sample in the canister can be diluted to bring it into the range of the calibration curve. The formaldehyde samplers are analyzed using the National Institute of Occupational Safety and Health's (NIOSH) chromatropic acid method, where the formaldehyde is removed by aqueous extraction and then reacted with chromotropic acid to produce a color, which is measured by a spectrophotometer. The typical range of results for selected compounds along with the method detection limits for these analyses are shown in Table 1.

Quality assurance (QA) techniques are used to ensure the validity of the final results from the sample analyses. In addition to the stringent QA requirements stated in the TO-14 methods, the Toxicology Laboratory employs several recognized means of ensuring sample integrity. Prior to delivery for a mission, the GSC containers are dosed with three surrogates that span the volatility and polarity range of expected compounds, and the recovery of these compounds is measured during the postflight analyses. Poor recovery flags the sample for investigation. In addition, lab controls are prepared when the mission samplers are readied and unused GSCs (contingencies) serve as trip controls. Finally, pressures are monitored from the time the GSCs are logged into the laboratory until all analyses are completed to determine if the sample valve or fittings are leaking. As in the preflight preparation of the GSCs, the SSAS tubes are each dosed with the same three surrogates. Sample volume through each SSAS tube is calculated by knowing the sample pump flow rate and the sample time. Consequently, it is important to verify that the flow rate did not change significantly during the flight, so the flow rates through each tube are measured before and after flight to ensure that the sample flow did not change significantly.

TABLE 1: Selected compound concentrations from Shuttle and ISS. Shuttle data are from STS-90, 96, and 103. ISS data are from 2A, 2A.1, and 2A.2b. Total number of samples averaged was 28. MDL=method detection limit and SMAC=spacecraft maximum allowable concentration.

Compound	**Avg. Concentration range (mg/m3)**	**MDL mg/m3**	**SMAC mg/m3**
Methanol	Trace - 0.42	0.05	9
Ethanol	Trace - 2.6	0.05	2000
Acetone	Trace - 0.20	0.05	50
Isopropanol	Trace - 2.0	0.05	150
Dichloromethane	Trace - 0.10	0.05	50
Freon 113	Trace - 0.06	0.05	400
n-Butanol	Trace - 0.25	0.05	80
Toluene	Trace - 0.18	0.05	60
Methane	Trace - 29.0	6.6	3800
Hydrogen	Trace - < 3.3	0.41	340

ADVANCED WORK

Improving the data arising from analyses of archival samplers involves advancing the art of sample acquisition and sample analysis. The Toxicology Laboratory endeavors to make strides in both these areas. Collecting a representative sample of the air on spacecraft has become more problematic as spacecraft have been expanded from one module (Shuttle) at $65m^3$ to many modules (ISS) at more than $350m^3$. Results from sampling, coupled with crew reports from the initial ISS flights, have clearly pointed to poor air mixing in areas of the ISS. During the Shuttle program, the air was assumed to be well-mixed and sampling results seemed to support that assumption. Efforts are underway to improve sampling strategies and to provide additional sampling and monitoring in suspected areas of poor air movement to ensure representative sampling in ISS.

Currently, the Toxicology Laboratory is evaluating a new inlet/preconcentrator system that potentially could increase the recovery of polar and very volatile organic compounds from the samplers. Other method development projects include assessment of shorter GC columns to decrease the analytical run time, and creation of a GC method to quantitate polar compounds (usually alcohols) when the sample concentration far exceeds the GC/MS calibration range.

Two ongoing projects to improve the sampling process are a study of silicosteel canisters and the development of the automated multisorbent tube air sampler (AMTAS). Silicosteel canisters are claimed to be more resistant to wall effects, consequently recovery should be improved for polar compounds, e.g., methanol, and other reactive substances, e.g., sulfur compounds. Testing is currently underway to verify that silicosteel represents an improvement over the Summa-treated canisters.

The AMTAS (Figure 3), a more ambitious project, is aimed at bettering the SSAS by automating most of the functions to minimize astronaut interaction during spaceflight nominal operations. The AMTAS, as the name implies, automates the archival sampling by preflight programming of the sampling regime for a particular mission. The

A **B**

FIGURE 3: Automated Multisorbent Tube Air Sampler (SSAS). A) Sampler with its 16 tubes. B) Sampler in desorb mode. After return to the laboratory, one tube is desorbed in the heater without risking the integrity of the other tubes or exposing the tubes to ambient air.

crewmember need only deploy the AMTAS in the cabin and the program will activate the sampler at the appropriate time and switch the valve to the correct tube for sampling. Subsequent sampling on other tubes is performed automatically and the AMTAS is deactivated at a preset time near the end of the mission. In the event of a contingency, a flip of a switch puts the AMTAS in the manual mode so a crewmember can match sample parameters (flow rate, sample time, etc.) to the situation. The AMTAS contains 16 tubes, which provides the means to collect more samples than the SSAS during longer missions and provides the flexibility to collect reactive compounds such as formaldehyde or ozone by filling some tubes with special sorbents.

Work in the future will focus on the miniaturization and further automation of archival sampling hardware to maintain or enhances performance.

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A New Technique for Long-Term Monitoring of Airborne Contaminants

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ABSTRACT

This paper describes a long-term passive monitor to measure trace concentrations of airborne contaminants. Although active systems for air sampling have many advantages and are the current reference method, they have many disadvantages too. Passive sampling's advantages are simplicity, ease of use and maintenance, cost, power consumption and space. Disadvantages are that they are susceptible to environmental parameters of air motion, reverse diffusion of adsorbed compounds, they do not give a real time output, and, they require very careful validation. Passive sampling monitors are being used more frequently as personal dosimeters for the 8-hour working day but have never been considered as "long-term" (greater than 12 hours) integrating monitors. Naval Submarine Medical Research Laboratory (NSMRL) has embarked on a passive monitoring program and developed a validation program to establish that the passive monitor can be a reliable long-term airborne contaminant monitor.

Key Words: Air Quality Monitoring Risk Assessment Passive air samplers

INTRODUCTION

The Submarine Atmosphere Health Assessment Program (SAHAP) was established in March 1995 and is located within the Department of Operational Medicine at the Naval Submarine Medical Research Laboratory at Submarine Base New London in Groton Connecticut. The SAHAP team takes the view that the operating submarine may be regarded as a "complex chemical engine" which creates a unique mixture of compounds that are of interest to Naval operational, medical, occupational hygiene, design engineers, and materials control personnel. A submerged nuclear submarine is an enclosed space with a confined and limited atmosphere that usually lacks external ventilation. Submarines represent a unique environment, in which individuals work and reside for several months. Since the mission of the submarines requires long periods of submerged, breathing air must be generated, regenerated and cleaned to avoid affecting the health and well being of the crew, and performance of electrical and mechanical systems. A nuclear submarine is therefore a non-traditional workplace, where continuous exposures can last 90 days. During these deployments, the submariners are potentially at risk of exposure for 2100 hours or longer. If, for example, retrospective air samples were collected for several hours every three days, this would represent exposure information for less than 10% of the deployed period.

There are many sources of air contaminants within submarines, and there is a potential for increased contaminant concentration with time during "hatch closed" operations. The mixture results from a combination of: human metabolism, off gassing of construction materials and materials brought onboard, and production of contaminants from the mechanical systems. The U.S. Navy has developed a series of time weighted average, 90-Day Limits to deal with the unusual nature of submarine duty. These existing limits are:

- 1-hour emergency exposure limits
- 24-hour limits, continuous exposure limits
- 90-day limits.

CHOICE OF SAMPLING METHOD

Active sampling involves the forced movement of air, generally by an electrical or battery driven pump, across or through some collection device. Solid sorbent tubes, treated or untreated filters, and liquid media are common collection techniques. The primary advantage to active sampling is that many of the reference analytical methods published by the National Institute of Occupational Safety & Health (NIOSH), Occupational Safety & Health Administration (OSHA), and American Society for Testing and Materials (ASTM) have had extensive evaluation and proven reliability .

Grab samples are air samples that are taken to evaluate airborne contaminants at a single point in time. Common methods of grab sampling include detector tubes, evacuated flasks, polymeric bags, syringes, and direct reading instrumentation. Grab samples are useful to identify higher concentrations of certain air contaminants and to provide preliminary hazard information but for the most part, they do not integrate the amount of contaminants detected over time. Detector tubes are used on-board as a qualitative spot check of submarine air quality (SAQ) and CAMS operation and are grab samples.

Passive Air Sampling Passive samples are collected by diffusion. Since small molecules diffuse faster than large ones, the diffusion coefficients for different analytes are a function of molecular dimensions. Specifically, the two-dimensional (Fickean) diffusion rate will be directly proportional to the average cross-sectional area presented by the molecule in the plane perpendicular to the direction of diffusion. Since molecules rotate freely in the vapor phase, the average cross-sectional area presented by a vapor molecule corresponds closely to a parameter, which may be called the molecular cross-section. There are several design consideration for a diffusive sampler. The inlet to the diffusive sampler contains a sampling grid that provides a fixed diffusion layer to provide a reliable air sampling rate. The sampling grid is injection-molded polypropylene, and is dimensionally reproducible, non-contaminating, inert, and non-sorbing with respect to a variety of organics.

As with solid sorbent tubes, diffusive samplers are available in a wide range of sorbent media depending on the sampling needs. SAHAP uses diffusive samplers for ozone, aldehydes and ketones, volatile organic compounds, and nitrosoamines. Some of these monitors are designed specifically to meet SAHAP's need for long-term sampling. These monitors are commercially available, and will prove useful for any air quality surveys requiring long averaging times.

The SAHAP is engaged in a program of passive monitoring in USN submarines and is currently validating the monitors against other methods.

Microbiological Investigations of the Mir Space Station and Crewmembers During the International Space Station Phase 1 Program

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From 1995 to 1998, the National Aeronautic and Space Administration (NASA) has worked in cooperation with the Russian Space Agency in joint missions aboard the Russian space station, Mir. These NASA-Mir missions offered a variety of unique opportunities, including the ability to observe the relationship between humans and microbial flora in a closed, controlled ecosystem. For NASA, this joint venture also provided insights into the microbial ecology occurring within a closed chamber subjected to microgravity. The microbial flora in the air aboard Mir was surveyed from NASA missions 3 to 7 to characterize the dominant flora and assess the efficiency of the air filtering systems.

The air processing system aboard Mir, The POTOK 150M, was designed to remove up to 4 to 10 kg free-floating condensate per minute from the air before further processing. A fibrous, granular filter approximately 10 micrometers in depth initially removed large particles and certain chemical contaminants at the intake of the system. A hydrophilic, porous plate separator followed this initial filter removing condensate from the air by drawing off water through channels in the plate. A negative pressure in the channels was provided by a diaphragm pump that collected condensate for delivery into a regeneration system. The plates were designed to remove water at concentrations up to 10% of the total air volume. Over time, the plate efficiency would decline and require replacement as the channels were clogged by particulate material and microbial growth. In the event of a system failure, the air/condensate was vented back into the main cabin. After condensate removal, the air was circulated through a system of combined electrostatic precipitators (1). Microorganisms and small aerosol particles were electrostatically attracted and sequestered on the surface of precipitators by mechanical entrapment and electrical attraction forces (1).

NASA has two primary concerns regarding changes to the microbial flora within the station. The first is the possible increase in medically significant organisms in confined systems, especially those with mechanical systems that regenerate air and water. The second concern is the changes that may occur to the microorganisms and human immune system during flight. Low gravity and low shear studies on bacteria have suggested a variety of physiological differences (4, 5), an increased number and distribution of potentially pathogenic microbes (2) and increased virulence (6). When combined with a putative blunting of the immune system (3, 7, 8), this evidence suggests an increased risk of infectious disease in the crew during a long mission. The potential for infectious disease and the difficulty in system remediation during flight have compelled NASA to maintain a requirement for heterotrophic bacteria in air of 1000 colony forming units (CFU)/m^3 and maximum fungal concentrations of 100 CFU/m^3. These specifications have been maintained for the International Space Station (ISS) though the preflight specifications have been lowered to of 300 heterotrophic CFU/m^3 and 50 fungal CFU/m^3.

MATERIALS AND METHODS

Sample Sites. Air sampling sites were selected to maximize information gained about several key areas within the station. The sites selected were the control panel in the core module, the dining table, the commander's cabin, and the Kristall module hatch.

Microbial collection and enumeration. Air samples were collected inside the chambers with a Burkard air sampler (Burkard Manufacturing Co. Ltd., Hertfordshire, England), which impacted 84.9 liters of air onto either trypticase soy agar (Remel, Lenexa, KS) for bacteria or rose bengal agar (Difco, Ann Arbor, MI) for fungi [Figure 1]. Plates were incubated at ambient conditions (25 to 35°C) for 48 hours before bacterial enumeration. Rose bengal agar plates were incubated for 5 days to determine fungal concentration.

Microbial identification. Upon return to earth, viable bacterial cultures from air sample plates were subcultured and incubated on blood agar at 37°C for 48 hours. All bacterial colonies were identified using either a Biolog Automated Identification System (Biolog, Hayward, CA) or a Vitek Identification System (bioMérieux, Hazelwood, MO). Fungal cultures were subcultured on Sabouraud Dextrose Agar and incubated at 25°C for 5 days. Fungi were identified microscopically by their morphological characteristics.

RESULTS/DISCUSSION

Air sampling aboard Mir was designed as a study, rather than an operational function. Thus, sampling times and availability were based around the operational functions of the crew. From NASA 3 through NASA 7, 20 air samples at four locations were collected. Bacterial concentrations generally remained at or below NASA specifications [Figure 2]. The bacterial concentrations averaged 584 CFU/m^3 at the control panel, 525 CFU/m^3 at the dining table, 409 CFU/m^3 at the captain's cabin, and 98 CFU/m^3 at the Kristall module hatch. On two separate occasions, once at the captain's cabin and twice at the control panel, bacterial levels increased dramatically exceeding the NASA specification of 1000 CFU/m^3. The events leading to this increase were never revealed, and the problems were not chronic as bacterial levels returned within specification at subsequent time points.

Bacterial identification indicated no medically significant species [Table 1]. Due to the delay in return of samples, a small percentage of organisms were non-viable upon return. No specific flora was dominant, though the source of most could have come from the crew, the water supply, and the general cargo.

Fungal contamination remained above the NASA specification, 100 CFU/m^3, at all sampling sites for most of the missions [Figure 3]. The fungal concentrations averaged 240 CFU/m^3 at the control panel, 225 CFU/m^3 at the dining table, 216 CFU/m^3 at the captain's cabin, and 341 CFU/m^3 at the Kristall module hatch. The NASA maximum specification was exceeded during 75% of the sampling time points for the control panel and the dining table averaging. The captain's cabin exceeded specification 70% of the time and Kristall module hatch exceeded specification 74% of the time. The cause of the high fungal levels was not determined. Crew activity levels could be responsible for the high counts, though this would not explain a correspondingly low level of bacteria as displayed at the Kristall Module Hatch.

Fungal identification indicated no medically significant genera [Table 2]. As with the bacterial samples, the delay in return of samples caused a small percentage of organisms to be non-viable upon return. The dominant fungal flora were *Aspergillis*, *Cladosporium*, and *Penicillium* species. The sources of the fungi are not clear, though the crew and cargo are the most likely cause of contamination.

These studies support the potential of long-term space flight and that an environmental equilibrium between humans and microbial flora can be maintained. The bacterial and fungal contamination levels and the diversity are similar to the conditions found on earth. No difference in microbial characteristics was observed as a result of the closed system or microgravity. However, long-term microbial contamination is suggested by high fungal concentrations. While no medically significant fungi were present, the evaluation did not include the effect of fungal spores as allergens. In addition, these studies represent only a relatively few number of samples. The number and diversity of organisms found during flight suggest that analysis of samples should continue on board the International Space Station in order to support the success of the mission and health of the crew.

Figure 1. Astronaut Jerry Linenger prepares the Microbial Air Sampler (MAS) for use aboard the Mir Space Station.

Figure 2. Bacterial contamination aboard the space station Mir.

Table 1. Bacterial flora isolated aboard the space station Mir.

NASA 3	NASA 4	NASA 5	NASA 6	NASA 7
Acinetobacter calcoaceticus	*Aeromonas* sp	*Micrococcus* sp	*Bacillus* sp	*Bacillus* sp
Aerococcus sp.	*Bacillus* sp	*Sphingomonas paucimobilis*	*Staphylococcus aureus*	*Corynebacterium* sp
Bacillus sp.	*Chryseobacterium meningosepticum*	*Staphylococcus aureus*	*Staphylococcus* sp, not *aureus*	*Pasturella haemolytica*
Corynebacterium sp.	*Comamonas testosteroni*	*Staphylococcus* sp, not *aureus*		*Pseudomonas fluorescens*
Enterococcus faecalis	*Micrococcus* sp			*Serratia* sp
Flavobacterium meningosepticum	*Pseudomonas putida*			*Staphylococcus* sp, not *aureus*
Micrococcus sp.	*Sphingobacterium spiritovorum*			*Stenotrophomonas maltophilia*
Pantoea agglomerans	*Sphingomonas paucimobilis*			
Pseudomonas fluorescens	*Staphylococcus aureus*			
Staphylococcus sp, not *aureus*	*Staphylococcus* sp, not *aureus*			
Streptococcus sp, not *pyogenes*	*Streptococcus intermedius*			

Figure 3. Fungal contamination aboard the space station Mir.

Table 2. Fungal flora isolated aboard the space station Mir.

NASA 3	NASA 4	NASA 5	NASA 6	NASA 7
Aspergillus sp, not *fumigatus*	*Aspergillus* sp, not *fumigatus*	*Aspergillus* sp, not *fumigatus*	*Aspergillus* spe, not *fumigatus*	*Acremonium strietum*
Cladosporium sp.	*Candida* sp.	*Candida famata*	*Brevicaulis* sp.	*Aspergillus* sp. not *fumigatus*
Penicillium sp.	*Cladosporium* sp.	*Penicillium* sp.	*Chaetomium* sp.	*Candida guillermondii*
Yarrowia lipolytica	Hyphomycete		*Cladosporium* sp.	*Cladosporium* sp.
	Lypomyces sp.		*Mucor* species	Hyphomycete
	Paecilomyces sp.		*Penicillium* sp.	*Paecilomyces* sp.
	Penicillium sp.		*Rhizopus* sp.	*Penicillium* sp.
	Scopulariopsis brevicaulis		*Scopulariopsis* species	*Rhodotorula rubra*

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Exhaled Breath Analysis of Submariners from Diesel-Electric Submarines

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Summary

Exhaled breath concentrations of total volatile organic compounds (VOCs) of submariners from the Oberon class submarines was found to be substantially higher than that of the Collins class submariners reflecting the air quality and configuration of the two classes of submarines. The technique was also found to be sensitive to the work locations (forward and after compartment) of the crew in the Collins class submarines. Comparisons with a limited number of aircraft maintenance workers indicated higher exhaled breath concentrations of VOCs in Oberon submariners compared with Collins class submariners despite significantly higher air concentrations to which the aircraft workers were exposed.

Introduction

The use of pollutant air concentrations as an indicator of exposure hazards to humans does not take into consideration dermal absorption and assumes that exposure time is known. In many cases the subjects are mobile in areas where the nature and concentrations of air contaminants vary widely. Ultimately it is the amount of pollutants absorbed by the human body which will determine the toxicological effects.

Submariners are exposed to a plethora of air contaminants in an enclosed atmosphere for the duration of the mission which may vary from a few days to several weeks (Dibben 1993). The submarine atmosphere may contain small quantities of carbon monoxide, refrigerant gases, solvents, hydraulic fluid vapours and diesel vapours. The determination of the organic components is particularly challenging because of the complexity of the mixture. The toxicological effect of these substances will depend on the time spent by the subject in any particular location within the submarine and the nature and concentration of the air contaminants at that particular location.

The Royal Australian Navy operated 2 classes of submarines until 1999. The Oberon class has been in service since the 1960s and had no means of controlling the level of volatile organic compounds (VOCs) in the atmosphere. The major source of these is vapour from diesel fuel, lubricating oil, hydraulic fluid cooking and off-gassing of paints and other non-metallic materials. Over the years of service the internal surfaces of these submarines have become coated with oil and there is a fairly strong diesel type odour throughout the submarine. In the case of the newer Collins class submarines, there are two compartments, forward and after. The forward compartment contains the control room, galley and accommodation and the air conditioning system is fitted with a charcoal filter. As a result the two compartments have different air contamination profiles. Some crew members move freely between the two compartments while others spend most of their time in one or the other compartment. The crew spend 6 h on duty and 6h at rest in the forward accommodation quarters. Those working in the after compartment spend a maximum continuous time of 6 h in that compartment. While those on duty in the forward compartment spend all of their time in that compartment.

During the operation of the submarine external air is circulated through the boat (snorting), at different rates in different locations. The ventilation reduces the level of the atmosphere contaminants during these periods. As a result, air concentrations of pollutants vary periodically and because of the movement of submariners within the boat the measurements of these concentrations are a poor approximation of human exposure levels.

The absorption of air contaminants occurs principally through inhalation (but also through the skin) and subsequent partitioning between blood and air in the alveoli after which they are further partitioned between the blood, body tissues (fat, muscle) and organs (liver). Thus with a knowledge of the relevant partition coefficients it is possible to determine the concentrations of the pollutants in these locations from exhaled breath analysis (Wallace & Pellizzari 1995, Wallace *et al* 1996).

The application of exhaled breath, as a measure of exposure of submariners to Volatile Organic Compounds (VOCs) was first reported in 1984 (Knight). Given the potential of this technique to yield valuable exposure data, a methodology was developed for breath sampling of submariners and subsequent analyses by GC-MS in order to determine the body burden for organic vapours present in the submarine atmosphere.

A number of air quality trials have been conducted over the past 5 years, on both classes of submarines in order to compare differences in air quality and compliance with international submarine air quality standards. In addition, a survey of VOCs in the exhaled breath of submariners from Oberon and Collins class submarines was undertaken to determine their exposure to diesel vapour and other organic air contaminants and as a comparison of air quality in both classes of submarines.

Submarine air quality is often subjectively rated by submariners according to the intensity of the odour and the persistence of the odour on the body and clothing after going ashore. Although it is standard procedure to measure submarine air concentrations of VOCs this does not necessarily indicate absorption by the body and clothing. However, the latter characteristic could conceivably be related to the concentration and decay of VOCs in exhaled breath.

2. Experimental

Sampling Procedure

Fused silica lined 1.8 L air sampling canisters, supplied by Entech Corp., USA, fitted with valves (Parker), were cleaned using an Entech model 3000 SL canister cleaning apparatus. The valves were then closed and the inlets were capped with Swagelock fittings. Breath samples were taken from non-smoking subjects within 15 minutes (unless otherwise stated) after emerging from the submarine. The subjects were fitted with a nose clip and supplied with purified air, on demand, from a charcoal filtered air supply (Breath-Easy) through a mouth piece in an arrangement similar to a Scuba system. The airways and lungs of the submariners were first purged with the filtered air prior to breath sampling.The cap from the valve inlet was removed and a 10 cm Teflon tube containing a 1 μm filter (Whatman Polydisc TF) was fitted to the inlet to avoid bacterial saliva contamination of the canister. The tube contained an insert to restrict the air flow so that when the valve was fully opened it would take approximately 15 s to fill the evacuated canister. The subject inserted the tube into the mouth and opened the valve allowing the canister to fill with air from the subject's lungs. The canisters were then pressurised to 207 kpa with dry helium. A portion of the canister sample (100 ml - 400 ml) was then introduced into the Entech model 7000 Preconcentrator and introduced into the gas chromatograph (Fisons, 8000 Series) coupled to a quadrupole mass spectrometer (Fisons Trio 1000).

Analysis

Breath samples (400cc) were concentrated using the Entech 7000 pre-concentrator. Each sample analysis also included the addition of an internal standard of d^8 -toluene (100cc) during the pre-concentration cycle. The unit uses two pre-traps , one for the removal of water (~50%RH: glass beads at -10°C) and the second for concentration of the sample (Tenax at -60°C) and removal of CO_2 (~2%), which passes through the trap. After reheating the first trap to 20°C, and purging any volatiles from it on to the second trap, the Tenax trap is then back flushed and thermally desorbed (180°C for 3.5 minutes) onto a on-line cryogenic trap (-150°C) for focussing and injection onto the GC column.

The samples were chromatographed on a SGE 50m, 0.32mm I.D., 3 micron BPX5 column. Helium was used as a carrier gas at 140 kpa. GC oven conditions were 2 minutes at 35°C, then heated to 85°C at 15°C/min, then to 150°C at 4°C/min, and finally heated to 200°C at 2°C/min and held at this temperature until the chromatography was complete.

3. Results and Discussion

Exhaled breath samples of 75 submariners, from Oberon and Collins class submarines, were collected between November 1998 and December, 1999. These were analysed for the presence of organic compounds. Submarine whole air samples were also taken on each occasion and analysed by GC-MS.

The two classes of submarines are similar in that they have the same sources of air contaminants but the configurational differences affect the concentration and distribution of VOCs within the submarines. Peak concentrations of VOCs in the engine room of both classes of submarines were found to be comparable reaching peak levels of 30-50 ppm in the engine room after the engines had been stopped. In this situation there is no intake of fresh air through snorting and the radiated heat from the engines results in the volatilisation of diesel fuel in and around the fuel lines.

Because of the isolation of the forward compartment and the air filtration, the VOC concentrations in the forward compartment of the Collins class submarines do not exceed 1 ppm and they consist of more volatile compounds such as butane, isobutane, dichloromethane (Figure 1). By contrast, VOCs in the after compartment consist mainly of diesel hydrocarbons (Figure 2).

In the case of the Oberon class submarines there is a relative free flow of unfiltered air throughout the boat. The VOCs are largely due to diesel hydrocarbons and their composition is fairly uniform throughout the boat with a minimum concentration of 10 ppm and maximum peak concentrations of 50 ppm in the engine room.

Comparisons of air samples with exhaled breath samples of submariners from both classes of submarines showed relatively higher concentrations of the more volatile compounds in the exhaled breath (Figure 3). The major contributing factors could be the sorption of the less volatile compounds on the canister surface at the low exhaled breath concentrations and the lower solubility of these compounds in blood.

Exhaled breath samples from Collins class submariners who worked in the after compartment ("mechanics" and "stokers") showed a subtle but consistent difference when comparing the relative concentrations of 5 prominent hydrocarbons such as methyl cyclohexane, octane, nonane, decane and undecane (Figure 4). These subjects had proportionately higher concentrations of nonane, decane and undecane in their breath, consistent with the presence of these compounds in diesel fuel. Overall there was not a great difference in the total exhaled breath concentration between those with duties in the after compartment and those who spent most of their working time in the forward compartment (Figure 5, f &g, h&i).

When total VOC concentrations of exhaled breath from Collins class submariners were compared with those from Oberon class submarines the latter were found to be significantly higher reflecting the poorer air quality (Figure 5). The main reasons for this difference is the isolation of the engine room and location of the accommodation in the relatively clean environment of the forward compartment of the Collins class submarines. where the "mechanics" and "stokers" are able to eliminate VOCs from their bodies through their skin and lungs in a relatively clean atmosphere.

Exhaled breath samples were generally taken on deck but a number were also taken in side the Oberon submarines using the Emergency Air Breathing system (with the addition of a charcoal filter) to purge the air passages and lungs prior to sampling the alveolar air. This approach was designed to overcome the elimination of VOCs through exposure to ambient air prior to sampling as was the case with breath samples taken on deck. As expected, the results indicate a higher mean concentration of total VOCs measured by the inboard protocol (Figure 5, m,n,o). The large range of VOC concentrations (250-1380 ppb) for trial (k) is surprising, indicating a factor of 5 in the variation of exposures encountered within one submarine.

As exhaled breath analysis is not applied extensively to occupational exposure, there is a paucity of data from the industrial work place. The most relevant data are from aircraft maintenance workers and refuelers. Thesamples had been taken approximately 1 hour after completion of their duties compared with 15 minutes in the case of the submariners who were sampled on deck. The total exhaled VOC concentrations for these workers are significantly higher that those of the Collins submariners, but less than those of the Oberon submariners. It is interesting to note that the air concentrations endured by some of the workers (Figure 9, a,c) are almost 10 times that of the Oberons. This indicates the contributions of air concentrations and exposure time, as the aircraft maintenance workers have 16 hours respite from exposure during which much of the VOCs can be eliminated.

4. Conclusions.

The use of exhaled breath measurements is a sensitive and useful procedure for determining human exposure to VOCs in the submarine environment. The data reflect the difference in air quality between the new Collins and older Oberon class submarines and are consistent with subjective assessments. Comparisons with a limited amount of data from aircraft maintenance workers exposed to paint solvents and jet fuel suggest that the amount of VOCs absorbed by the Oberon class submariners may have been higher even though the air concentrations were comparable. At this stage there is insufficient knowledge on the subject to determine any health implications associated with these levels of VOCs in the exhaled breath of submariners.

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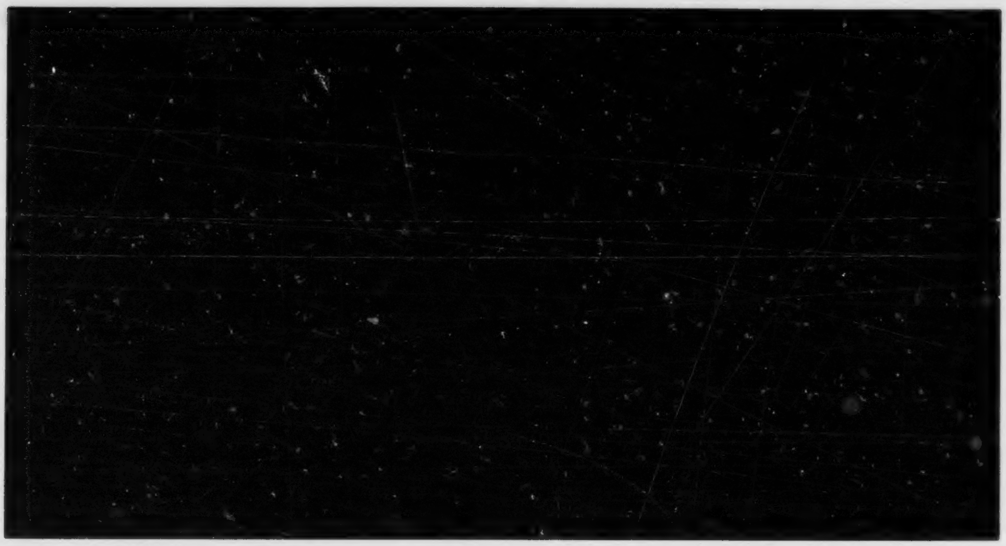

Figure1. Gas chromatogram of a whole air sample from the forward compartment of the submarine.

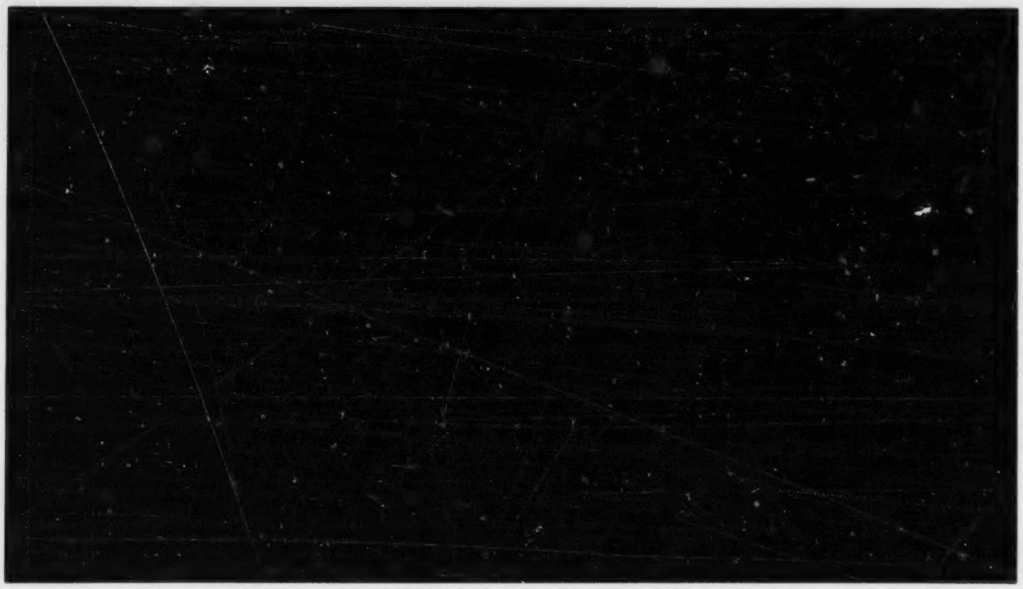

Figure 2. Gas chromatograph of a whole air sample from the after compartment of the submarine.

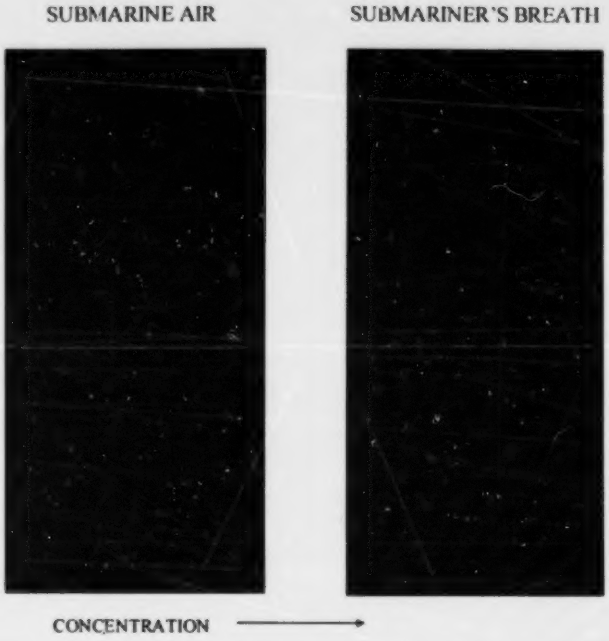

Figure 3. Comparison of composition (gas chromatographs) of whole air sample from an Oberon submarine with exhaled breath from an Oberon submariner. Acetone and isoprene are normally present in exhaled breath.

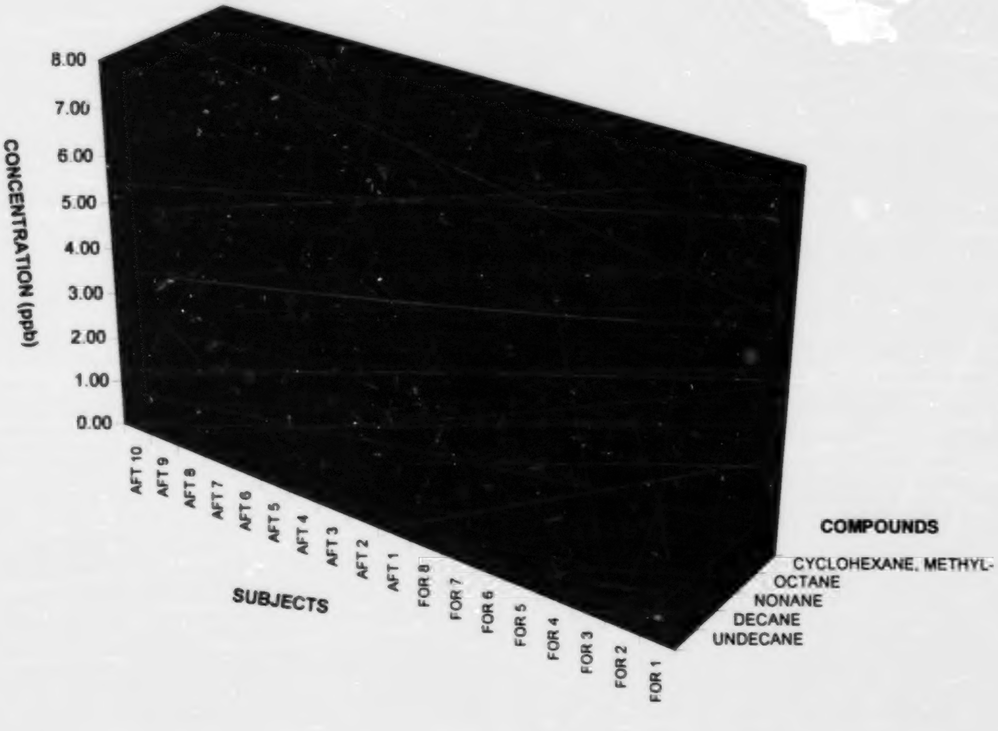

Figure 4. Exhaled breath results from Collins class submariners using 5 hydrocarbons as markers for the forward and after compartments.

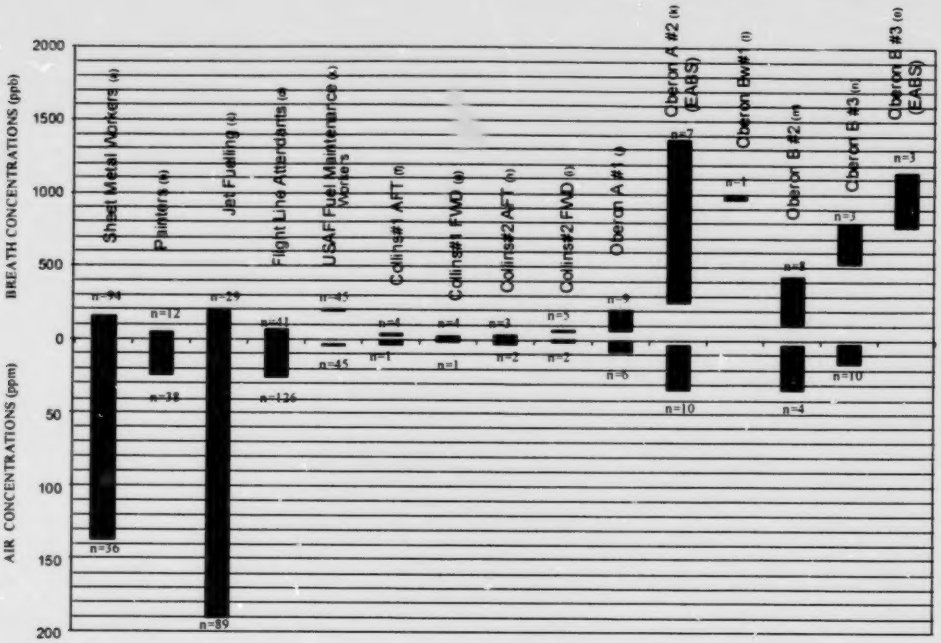

Figure 5. Total VOC concentrations in exhaled breath samples of submariners and aircraft maintenance workers, showing range, mean concentration and number of subjects (n), (a-d, Lemasters, *et al.* 1997; e, Pliel, *et al.* 2000).

Genomic Analysis of Buccal Epithelium and Peripheral Leukocyte Samples from Air Force Jet Fuel Workers: Identification of Biomarkers of Exposure and Implications for Study of Diesel Submarine Crews

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ABSTRACT

Kerosene-type jet fuels are complex and variable mixtures of aliphatic and aromatic hydrocarbons but no exposure limits have hitherto been specified for JP-8 jet fuel. Chronic exposure to JP-8 and other kerosene-based petroleum distillates has been associated with renal, neurologic, pulmonary, developmental, immune, and cellular responses that may constitute toxicity. The first major study of the human health effects of acute occupational exposure to JP-8 is in progress and is a collaborative effort between the U.S. Air Force, the U.S. Navy and other government and academic institutions. In addition to a broad range of data from other endpoints being evaluated by collaborative organizations, pre- and post-exposure blood and buccal epithelium was collected from each subject for total ribonucleic acid (RNA) extraction. Although preliminary results suggest that RNA from both tissues is of acceptable quality for gene microarray analysis, collection of buccal epithelium has several advantages over blood collection, including a less invasive collection procedure. The results of the microarray analysis suggest that JP-8 induces differential expression of a multitude of genes in individuals occupationally exposed to JP-8. Furthermore, potential biomarkers of exposure may be identifiable once gene expression data is correlated with data from behavioral and physiological endpoints. These data may also provide the basis for a similar study of the health effects of diesel vapors and aerosols in submarine crews.

BACKGROUND & DISCUSSION

Kerosene-type jet fuels are complex and variable mixtures of aliphatic and aromatic hydrocarbons. The U.S. military is shifting from current fuels (JP-4 and JP-5) to the JP-8 formulation because of its relatively low vapor pressure and high flash point, resulting in enhanced fuel economy and decreased risk of fire or explosion. Within the Navy, the use of JP-8 jet fuel in surface fleet and aviation communities is also anticipated. Chronic exposure to JP-8 and other kerosene-based petroleum distillates has been associated with renal (1), neurologic (2), pulmonary (3), developmental (4) and immune responses that may be associated with toxicity (5). At issue is the question of how these responses may be employed as markers of toxicity. However, no nationally accepted occupational exposure levels (OELs) have hitherto been specified for JP-8 jet fuel. Potential exposure scenarios for Naval and Marine Corps personnel are numerous, including both shore- and ship-based flightline and other shipboard personnel. Within the

U.S. Department of Defense, JP-8 is recognized as the largest single chemical exposure, and current annual use of JP-8 in this agency exceeds 5 billion gallons.

Despite a lack of agreement on appropriate OELs, a preponderance of literature describing the health effects of JP-8 is available. The use of breath measures to determine body burden of jet fuel and jet fuel metabolites has been well-described and several studies have demonstrated significant differences in the concentration of various hydrocarbons in the breath (6-9). Likewise, several investigators report biological changes in occupationally exposed humans and in animal subjects. Genotoxicity (10), occupationally-related neurologic disorders and hearing loss (11), postural balance changes (12), changes in activity and expression of drug metabolizing enzymes such as glutathione-S-transferase (GST) (13), and changes in brain and serum neurotransmitter levels (14) have been reported in the literature. Alterations in expression of genes involved in DNA repair, drug metabolism, and cell signaling have also recently been described (15).

Recently, a major collaborative study was initiated to attempt to correlate ambient exposure with human body burden, neurologic performance measures, and other biological functions in Air Force jet fuel handlers. The research protocol design is a short-term prospective cohort study, with the "exposed" group consisting of Air Force personnel from each of seven CONUS Air Force bases who routinely perform maintenance activities requiring entry into the fuel tanks of jet aircraft. Moreover, to be included in the study, each subject must have experienced at least nine months of persistent jet fuel exposure via tank entry for 1 hour at least twice each week. The unexposed personnel group consists of Air Force personnel who do not routinely work with or have exposure to fuels or solvents and are stationed on the same base as the exposed group. Personal air sampling, grab sampling, and constituent analysis of raw jet fuel from each base in the study comprise the basic industrial hygiene measurements. Included among the performance health measures are a series of computer-based neurobehavioral tests designed to measure motivation, response speed, coordination, grip strength, complex mental functioning, memory, and attention. Postural sway is being recorded to test the subject's control mechanism for governing balance and the conditioned eyeblink response measures more global issues of brain functioning. Risk factor and medical records reviews are also performed. Biological measures include internal temperature monitoring, blood GST expression and activity, GST genotyping, benzene and naphthalene urinary metabolite analysis, breath sampling for benzene and naphthalene, and skin exposure sampling at known sites of exposure.

Another biological measure in this study includes an analysis of jet fuel-induced changes in expression of genes. The development of gene microarrays, or "gene chips," over the past five years has resulted in the ability to measure changes in the activity of thousands of genes simultaneously. Prior to the availability of this technology, evaluating the expression of even one gene at a time could take as long as two weeks. In sharp contrast, the gene chip approach allows the simultaneous analysis of thousands of genes over the course of a few hours, providing a more rapid, "global" view of the effect of stressors on the biology of cells and tissues. Although genes are expressed differentially among distinct cell and tissue types, requiring restriction of interpretation to the tissue type sampled, gene expression between several tissue types can be compared. In this study, we examine the activity of genes from peripheral blood leukocytes and epithelial cells taken from a cheek swab from subjects in the Air Force jet fuel study. Although data collection is incomplete (subjects from six of seven bases have been sampled) and data analysis will not be complete for several months, preliminary results suggest that occupational exposure to jet fuel vapor results in changes in several performance and biological parameters, including substantial changes in expression of genes involved in cell signaling, DNA repair, and toxin metabolism. Ultimately, we wish to correlate changes in buccal epithelial gene expression with changes in performance. Results from the study should help elucidate the impact of occupational exposure to JP-8 on health and performance and begins to build a basis for developing a rational JP-8 exposure standard.

Although the diesel submarine atmosphere is fundamentally different than an aircraft hanger, the presence of diesel vapors and aerosols in diesel boats is an exposure analogous to that experienced by jet fuel workers. However, application of the experimental design described above to a similar study in diesel submarine crews would be difficult because of the large logistical footprint required for collection of data from all parameters being examined. For example, the Air Force jet fuel study requires no fewer than 20 to 25 highly trained personnel to collect samples and data at each base. Likewise, many of the parameters being evaluated rely on multiple items of equipment that have specific electrical, space, and temperature requirements. Clearly, the logistical requirements of such a study applied to sailors on diesel submarines underway is incompatible with the routine operation of the boat. However, analysis of changes in gene expression, if validated as a predictor of changes in performance, could use resources already present on any submarine. With the exception of a small amount of equipment and trained personnel required for sampling of diesel vapor/aerosol while underway, no additional equipment or personnel would be required. Blood or buccal swab sampling could be accomplished anytime underway by a member of the boat's medical department and preserved for analysis until the boat returns to the pier. Sample analysis would be accomplished by a qualified laboratory once the samples were collected from the boat.

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This research has been conducted in compliance with all applicable Federal Regulations governing the Protection of Human Subjects in Research.

APPLICATION OF THE GLOBAL ASSESSMENT SYSTEM FOR HUMANS (GASH) TO EVALUATION OF SUBMARINE ATMOSPHERE EXPOSURE EFFECTS

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ABSTRACT

The Global Assessment System for Humans (GASH) is a computer-based tool being developed at NHRC-TD, Dayton, OH to provide rapid field evaluation of the performance (military readiness) capacity of personnel, including following exposure to chemical toxicants or stressors. At present, a GASH prototype is being utilized to evaluate the neurobehavioral capacity of 165 military personnel exposed repeatedly to JP-8 jet fuel and 165 matched controls at six domestic Air Force bases. These personnel, evaluated before and following 4-hr occupational exposures, are being measured for several physiological parameters, ability to learn a conditioned eyeblink response, and on multiple tests of motor & sensory system, motivational and cognitive capacity. The GASH, when completed, will be available for acute, acute/chronic, and chronic evaluation of submariners before, during, and following repeated submarine assignments lasting up to 6 months. Additionally, the GASH may prove useful in screening of personnel for extended submarine duty. A proposed application of the GASH is evaluation of the performance consequences of submariners exposed to DBNP, the "yellow submarine" chemical. Due to the possibility of atmospheric contamination aboard submarines during underway missions, it is believed that the GASH represents a significant contribution to both evaluating the health status of submariners and to ensuring the performance readiness of deployed submarine crews.

INTRODUCTION

The performance readiness of submarine personnel is critical globally to international defense, and locally to protection of mission-essential vessels, materiel and staff. The appropriate selection and assignment, training capacity, and "hour-to-hour" performance evaluation of personnel for submarine duty is perhaps more essential than for any other Navy operational scenario. Similarly, the performance capacity of jet aircraft pilots and support staff is an issue of significant importance to the readiness of the US Air Force. Because these mission-critical personnel are routinely exposed to a myriad of chemical toxicants and stressors during combat-related, as well as routine daily assignment, the need for a tool to evaluate acute and long-term changes in performance capacity is amplified. On submarines, in which crewmembers are exposed to a recirculated breathing atmosphere for as long as 70 days, the possibility for changes in performance capacity due to changes in the quality of this air supply is very great. Most obviously, combat or damage control scenarios can result in addition to the submarine atmosphere of fire gases or other severely neurotoxic chemicals. More subtly, exposure to off-gassing of routine materiel, unpredicted interactions among normal atmosphere constituents, or interactions between innocuous constituents and air treatment systems can result in acute or persisting performance decrements that may be difficult to detect, but are sufficient to reduce submarine crew efficiency.

For these reasons, the Neurobehavioral Effects Laboratory (NEL) at Wright-Patterson Air Force Base has, since 1995, been involved in development, applications testing and validation of a comprehensive battery of tests to evaluate the performance readiness of critical military personnel including, but not limited to submariners and jet aircraft personnel. When completed, the Global Assessment System for Humans, or "GASH", will provide a rapid and cost-effective method for testing the performance capacity or readiness, respectively, of prospective or assigned submariners either shipboard or in a stateside environment. Consisting, at present, of a PC and several remote-sensing instruments, the complete GASH hardware system can be easily transported to any field, laboratory or hospital setting. Work in progress is developing a highly durable, miniaturized (Game Boy™ like) GASH hardware system that can be worn as a belt pack during performance of mission-critical assignments (i.e., sonar operation, weaponry control). Because virtually all operating instructions are provided to the subject on the GASH response screen, in one of several available languages, there is no need for extensive training of GASH testing technicians. GASH results, interpreted as a "percentage of maximal readiness," will be provided almost simultaneously with completion of testing to supervisory staff, allowing informed decision-making as to maintenance or replacement of specific personnel performing mission-critical tasks.

The GASH is superior to other existing human performance batteries, often engineered to evaluate clinical disorders, because it was designed specifically to identify deficits (or enhancements) that are known to impact military-specific task requirements. These areas have been identified as:

	GASH PERFORMANCE FACTOR SUB-AREAS
1	**General Neurological Activity**: Including Fundamental Excitatory Processes and Inhibitory Tone
2	**Motor System Integrity**: General Locomotor Activity, Muscle Strength, and Equilibrium
3	**Physiological Irritancy**: Sensory, Dermal and Respiratory Organs
4	**Sensory Acuity**: Visual, Auditory and Proprioceptive Systems
5	**Emotionity**: Frustration, Anxiety, and Depression
6	**Motivational Processes**
7	**Social Behaviors**
8	**Cognitive Capacity**: Including Learning, Memory, and Decision-Making

A GASH prototype is presently being used to evaluate possible acute and/or long-term changes in the performance capacity of USAF avionics personnel exposed repeatedly to jet fuel (specifically JP-8). One-hundred and sixty-five USAF personnel with known daily exposure to JP-8 vapor, aerosol and/or raw fuel for at least 4 months, as well as 165 military-matched controls, are being tested at 6 different domestic bases. Many of these exposed personnel are required to clean or repair the interior of aircraft fuel tanks resulting in unavoidable respiratory and dermal exposures. Unimpaired performance capacity of this cohort is obviously critical both to the readiness of services aircraft and the safety of aircraft flight crews and transported troops. Each exposed and control subject is being evaluated on nearly 30 physiological and neurobehavioral parameters both after a three-day rest from jet fuel exposure (chronic effects) and again following a 4-hr occupational exposure to JP-8 (acute/chronic effects). A summary of the JP-8 toxicity issue can be found in the article, "Toxic Fuel - Is JP-8 Getting Under Your Skin?", found in the 21 August 2000 edition of the *AirForceTimes*. Preliminary results of this massive testing protocol are expected to be available in December 2000.

Specifically, the GASH consists of the following tests:

1 - GENERAL NEUROLOGICAL ACTIVITY

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SAMAP 2000 - Proceedings

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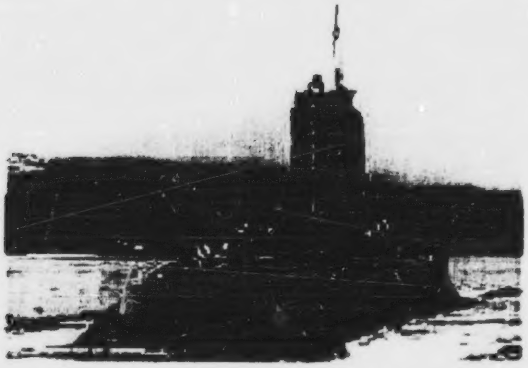
Part 3



Partie 3

SPASM 2000 - Actes

Troisième Conférence
sur la surveillance et la purification
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C.L. Wilson[1], S. Ryder[2,3], W. Horn[3], R.L. Carpenter[1], W.K. Alexander[1], and K.R. Still[1], [1]Naval Health Research Center Detachment (Toxicology), Wright-Patterson Air Force Base, OH[2]Royal Navy Dockyard, Portsmouth, U.K. [3]Naval Submarine Medical Research Laboratory, Groton, CT. USA.

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Nathalie R. Bernier[1], Sylvie Fradette[1], Kenneth G. Johnson[2], Mark Johnson[1], Carmen Parent[1], Michelle Plante[1], and Peter A. Rogers[1], [1] Systèmes EnviroBio Inc., 1400 boul de Parc-Technologique, #207, Québec, Canada, [2] Directorate S&T Human Performance, Defence R&D Canada, 305 Rideau Street, Ottawa, Canada

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S. van der Gijp, J. Albers, J. van Bokhoven, H. van Es[1], P. Feron[2]

TNO-PML, AA Rijswijk, Netherlands, [1]Royal Dutch Navy, DMKM, The Hague, Netherlands, [2]TNO-MEP, P.O. Box 342, 7300 AH Apeldoorn, the Netherlands.

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Christina Östberg[1], Hans Örnhagen[1] and Lutz Schauer[2] , [1]Defence Research Establishment, Defence Medicine, Hårsfjärden, Sweden. [2]Astrium GmbH Friedrichshafen, Germany.

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Pilot Plant Performance of an Amine Regenerative Scrubber

D. Eaton, Defence and Civil Institute of Environmental Medicine, Canada
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gash from a ship's bow may be a very effective flooding valve. The diving decompression tables are designed to give a low incidence of decompression sickness and even lower of deaths. A figure of 10% DCS and 1% deaths would not be acceptable for a diving table. In a S/m accident, where waiting for tower escape may mean that more may die from severe DCS, then rush escape could be the best choice.

The second set of problems relate to questions passed to the writer for an answer where a S/m has BIBS (built in breathing system) or emergency air breathing system (EABS) air that is outside the decreed specification and needs or wants to go to sea. A similar question was raised by the Royal Navy in a forum of medical officers with an interest in S/m escape. The question related to the origin of an equation in their guard book that suggested that crew would survive with a carbon monoxide of 200 ppm for a long period, and higher values if the oxygen pressure was higher than normal.

From these problems I became interested in the basic question, when does a S/m atmosphere become so contaminated it is likely to harm or kill the crew if they remain till rescue? One of the more common causes of contamination is a fire, so it is likely that there will be contamination by several substances.

The Decompression Problem

As mentioned, the first problem was an analysis of the risks of rush escape in the COLLINS Class S/ms. Rush escape is a method of escape where all the survivors in a compartment are pressurised together as the compartment floods. The may need a supply of fresh air because the air in the compartment may be toxic. A canvas twill trunk is attached to the hatch and is pulled down so it forms a cylindrical projection below the hatch. When the hatch is opened the twill trunk retains an air space for the occupants. The stand with their heads in this space until it is their turn to escape. Then they exit under the trunk rim and float out through the hatch. Fig 1 is a schematic diagram through an escape compartment.

The maximum depth of interest is probably about 60 metres to the air space, say 65-70 at the keel because of nitrogen narcosis. Is it likely that a damaged S/m will bottom at a depth where rush escape may be an option? The answer is yes because of the higher risk of collision in shallow water, where traffic is denser and going deep is not an option. Why not just use the tower? Because it may take longer, increasing the risk of DCS. Also there was no proof that the S/m would remain habitable for that period. For a COLLINS, there is probably greatest risk of damage from a vessel approaching from astern, hence the risk of damage to the tower area needs to be considered. So the first part of the answer was that there appeared to be a role for rush escape if it was possible.

A decision of what were the likely flooding times of the compartment was the next question. It was assumed that an incident that leads to a rush escape would be obvious to the command and their response would be to obtain maximum buoyancy by blowing and starting all pumps. If this kept the S/m on the surface for 15 minutes it was assumed that the crew would abandon her while on the surface. So the question becomes what net flooding rate overcomes the surface buoyancy + pumping in15 mins. The answer in this was 53 tonnes/ min.

From the assumed rate of water entry of 53 tonnes / min., it is calculated that it would take 77 mins to flood the bow compartment. A linear rate of pressurisation was assumed in making this calculation

A linear pressurisation profile against time was chosen after a small study. It was conducted as there was no agreement on the likely pressurisation profile. A simple model, with a 1.5 litre gas cylinder acting as a compartment was flooded in a manner simulating sinking from the surface by pressurising in a compression chamber. A small orifice served as the hole causing the flooding and a graduated reservoir indicated the volume of water in the compartment Fig 2 is a diagram of the equipment. The pressure was calculated from the volume of water in the cylinder. A sample pressure/ time graph is shown at Fig 3.

Other assumptions were it would take one minute to get rid of the hatch and then the crew of 55 would escape at a rate of six per minute, these are averages of several estimates by operators. This meant that the first man would have one minute at maximum pressure, the middleman, six and the last, 11 mins. Things are better for the last man if there are fewer survivors.

The risk of exceeding the standard decompression tables can be estimated for dives that are reasonably safe by consulting papers like Weathersby et al 1986. This suggests that if we exceed the decompression limits on the USN tables we have a 1-2 % chance of DCS. For higher risk dives we must look to animal results. This work suggests that the risk curve is probably bell shaped, with a peak at about 4 times the maximum no decompression limit dive. For example Dick et al compressed pigs to study the effect of decompression sickness. Their chosen profile was to 200 ft (60 metres) for 24 minutes. This is assessed to be about 5 times the maximum length of a no decompression dive, 33% of the pigs had no symptoms, 13% died and the remainder (54%) had DCS.

From this and other evidence the following risk levels for table violations was developed.

No stops needed	Minimal risk of DCS
1-2 x maximum no stops time	Low risk of DCS (<5%)
2-4 x maximum no stops time	Acceptable (<50% DCS,<10% dead)
4-6 x maximum no stops time	High risk (50-90% DCS, 10-50% dead)
6+ x maximum no stops time	Very high risk (90+% DCS, 50+% dead).

The human reports from S/m escapees lack information on the pressure profile. An example of interest is the crew of HMS/m POSIDON who escaped from 40 metres after being exposed to a pressure rising over about two and a half hours, they survived but were unwell. At least one pressurised tunnel worker is reputed to have spent 9 hours at a pressure equal to 18 metres without symptoms, so some do survive severe profiles.

A decompression calculation program (ANDI Dive Planner) was used to analyse the decompression profiles. This program was told the pressurisation profile and the time spent at maximum depth. It then calculates the decompression stops would be needed for that dive. The total decompression times given by the program was compared to the decompression tables to compare the stress of dive profiles. Fig 4 is a diagram of this process,

Decompression stress was estimated by comparison with the US Navy tables. For example, the USN air diving tables allow a 10 minute dive to 130 ft before decompression stops are needed. A 40 minute dive (that is 4 times a long as the maximum no decompression dive) requires stops for 35 minutes. If the program that calculates decompression stops said our submariner required more than 35 minutes of stops it was called a high risk escape.

From the use of this approach it was decided that there was a place for rush escape in the choice of options for escape. For depths shallower than 30 metres most should be able to escape without DCS. For deeper depths and longer flooding times the risk increases but only for flooding times of over 60 mins is the risk assessed as very high for the first man. Figure 5 is set of plots of risk against flooding time

A possibly concerning aspect of the problem was that there was a body of opinion within the RAN that rush escape would be the least likely option to be used. So it could be removed as we were providing tower escape as well as rescue. This is potentially betting a large number of lives against the chance that the S/m will provide an environment that will remain habitable for several hours after a major accident. A bet I would not like to take.

You will probably want to know if this sort of prediction could be made for escapees that had been pressurised for a longer period. In this context the term saturated is used. It is the diving medicine term for the condition where the subject is in equilibrium with the gases they are breathing and longer exposure will not increase the amount absorbed or risk of DCS. For humans it requires a dive longer than about 24 hours

Until recently there was no suitable data to comment on the risks of depressurisation from longer dives where the subjects would be at high risk. Now, American Navy work by Dromsky et al, with pigs as the subject, suggests that they have to be saturated at a depth of about 30 metres to induce DCS in half the animals. A result that is encouraging when most escape systems cannot keep the rescued people at elevated pressure for during rescue. It is not yet clear if these findings will be applicable to humans. Fig 6 is a summary of their findings

It is a big gain if they can be used because of the risks when escape or rescue is conducted from a pressurised compartment. Only with a saturation pressure of over 30 metres will deaths be expected. Only if they are deeper 130ft (40 metres) and decompressed to the surface, is there likely to be no survivors. This is an exciting result as most guard books would currently restrict people and discourage escape if the depth they are saturated to a depth of more than about 10 metres.

MPCs When at Risk?

The chemical limit problems to be discussed come from the point that the current limits are designed to prevent harm to everyone. It is suggested that there may be a need for a limit that may hurt but not cause long term damage. For example, the RAN 60 minute limit (MPC60) for carbon dioxide is 3%. But we expect the last survivor to escape with the carbon dioxide at 4.8 %. So they will be exposed to over 3% for about 10 hours.

Another example is carbon monoxide, the MPC 60 is 200 ppm. The work of Bloom suggests that 1600 ppm for 1 hour will produce about 30% carbon monoxide haemoglobin (CO Hb) in a resting person. Headache, confusion and breathlessness on exertion will be the likely result. In humans, 400 ppm of CO for 7 days produces about 40% CO Hb. A level that gives a serious poisoning, but it is suggested that it may be preferable to endure it than some of the alternatives. The examples chosen will give unpleasant conditions, but none of these are likely to be fatal to more than a small percentage of the crew. In the time that these conditions are endured some control measures might have been introduced. For example, operating the hydrogen burner and burning oxygen candles to raise oxygen pressure should help reduce the effects of the carbon monoxide.

In a fire there will be a complex mix of contaminants. The only study relating a large number of contaminants to survival that has been found was work on rats (Levin, 1996). It was designed to find how mixtures of toxic compounds interacted. For study purposes the combinations of interest were the mixtures that killed 50% of rats when they were exposed for 30 mins. Equations were developed that allow predictions of how different concentrations would interact.

It is probably more meaningful for this discussion to relate results to the RAN MPC 60 limits and to use an example that did not kill or incapacitate any of the 5 rats tested. It was shown that a mix of $1.6 \times CO_2 + 6.5 \times CO + 40 \times HCN + 20 \times NO_2$ was safe for these animals. In this example the numbers are the factor by which the MPC 60 has been exceeded. The paper cited also suggests that treating materials such as foams with cuprous oxide gives a reduction in the amount of toxic fumes produced, a point of possible interest in fitting out a S/m.

Conclusions

It is not intended to compare Navy people with rats or pigs, but ethics committees stop scientists poisoning people or giving large numbers severe DCS, even if they wanted to, so animals must be used. Some toxicologists think that a rat may be more susceptible to inhaled chemical poisoning than a human. Pigs are considered to be a reasonable model of a human for diving and decompression studies. So the findings discussed in this paper may indicate where the limits might be.

The important first question is do the crew need better guidance than given by the MPC tables and guard books? The answer proposed is yes, they may be faced with an uncertain chance of survival if they escape, so the may have a better chance if they remain in the S/m with a more toxic atmosphere than permitted with the current limits. The next question is how should the work be conducted? And what is needed in the S/m. It is suspected that more information on the toxicology of likely mixtures of toxic chemicals will be needed before any useful tool can be provided. This is likely to involve poisoning trials on larger animals, to get data that is more likely to relate to the effects on humans.

The decompression study discussed in the paper is presented as an example of how the risk of an unsafe procedure may be estimated.

FIG 1. A view through a schematic compartment after a rush escape. The crew rig the twill trunk,this provides an air space for their upper bodies while they wait to escape. They use the BIBS masks to obtain a supply of breathable air. When the S/m has flooded and the pressure inside is the same as outside, the hatch can be opened. In turn, the crew discard their BIBS, zip up their escape hoods, duck under the edge of the trunk and float to the surface.

FIG 2. The equipment used to investigate the relation between pressure difference and flooding rate. At the start of a run the cylinder is full of air at 1ATA and the reservoir is full of water. The recompression chamber is pressurised and water starts to move into the cylinder. The volume of water in the cylinder is measured. From this the volume of water, the amount of gas and the pressure in the cylinder can be calculated.

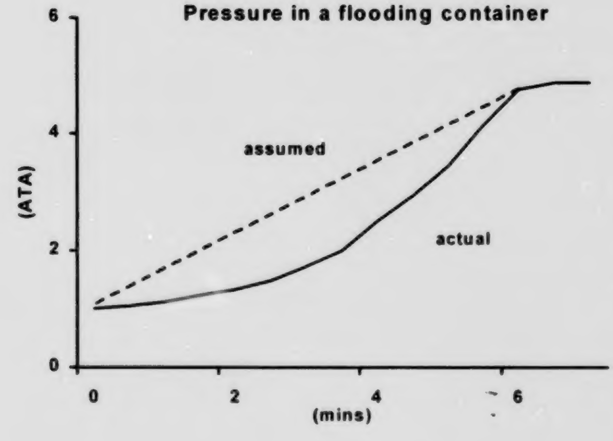

FIG 3. A pressurisation / time profile obtained using the equipment shown in Fig 2. From these results it was decided that a linear pressure rise would be assumed for calculating decompression.

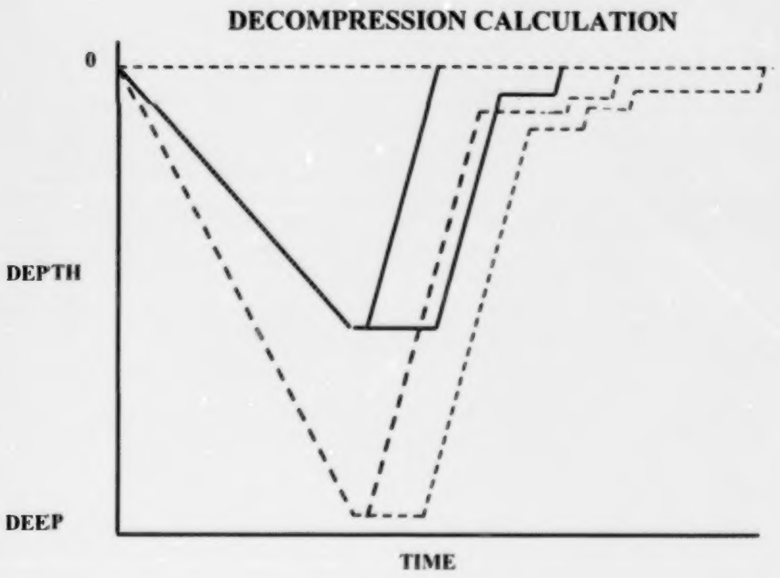

FIG 4. The decompression calculation program was told that the diver had done a linear pressurisation over the time on the x axis and then escaped (after 1 minute at maximum depth) or waited for 6 or 11 minutes. The program then calculates the decompression stops that should have been taken.

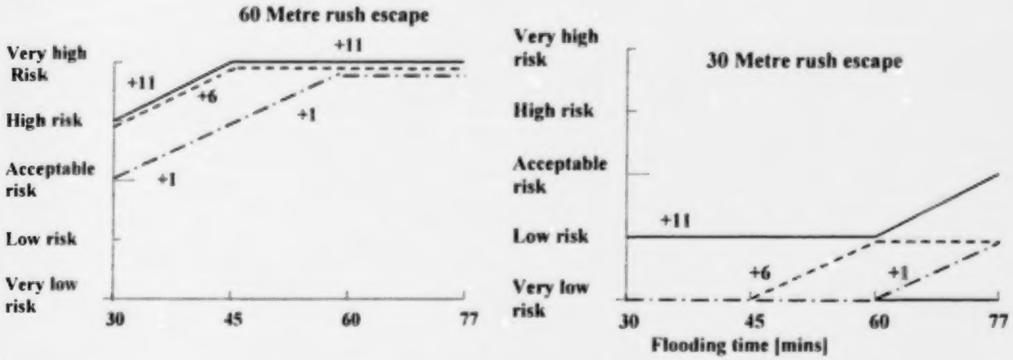

FIG 5. This shows the risk estimates for escapers leaving a S/m from 30 or 60 metres. The risk was estimated for divers with pressurisation times of 30,45,60 and 77 minutes and 1,6 and 11 minutes at maximum pressure, as shown by the lines marked +1, +6 and +11.

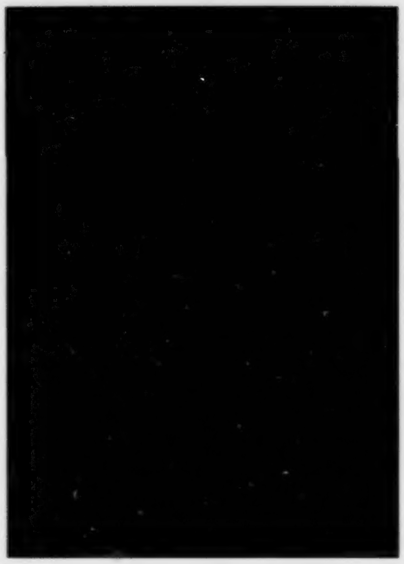

FIG 6. Estimates of the risk of DCS and death for pigs that had been given a saturation exposure. (From Dromsky et al)

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DEVELOPMENT OF ACTION LEVELS FOR TOXIC ATMOSPHERIC CONTAMINANTS IN A DISABLED SUBMARINE

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ABSTRACT

Despite the high standards of construction and operation of U.S. Navy submarines, a submarine casualty is always a possibility. The failure of a submarine pressure hull as a result of explosion, surface collision, grounding, or catastrophic failure would likely effectuate flooding and subsequent sinking of a boat. Events that might lead to the sinking of a submarine would possibly include fire or number of fires within the boat. As such, in addition to a plethora of other problems such as traumatic injuries, hypothermia, and pressurization, survivors would be forced to contend with toxic gases generated. The rapid buildup of these gases, combined with changes in atmospheric pressure resulting from breaches in the pressure hull, would require immediate action and constant monitoring. A Submarine Escape and Rescue Expert (SEAREX) system, an expert algorithm system for risk-based management of survivors in a disabled submarine, is under development by the Naval Submarine Medical Research Laboratory. Although the features of the full SEAREX program are beyond the scope of this presentation, a component of SEAREX designed to provide guidance in a toxic atmosphere scenario, the Toxic Gas Protocol, is based on two action levels: Submarine Escape Action Levels 1 (SEAL 1) and 2 (SEAL 2). SEAL 1 specifies limits below which survivors can remain in a compartment for a maximum period of 10 days, whereas gas concentrations at and above SEAL 2 require survivors to breath emergency air. The rapid resultant pressure increase from the use of EABs would force an immediate evacuation of the boat. Because of the risk inherent in the escape trunk egress and ascent phases of submarine escape, SEALs 1 and 2 have been developed and tentatively set at levels higher than those governing occupational exposure. The toxic gas management issue in a disabled submarine scenario also takes into account factors such as inadequate portable detection technologies, variability in compartment pressure, simultaneous exposure to multiple chemicals, and other sustained injuries. The major fire gases for which SEALs have been developed include carbon monoxide, hydrogen chloride, hydrogen cyanide, nitrogen oxides, sulfur oxides, hydrogen sulfide, chlorine, and ammonia. As a result of this very complex environment and the requirements for SEALs set far above occupational levels, tentative proposed SEALs have been forwarded for review by the National Academy of Sciences Committee on Toxicology and will be reviewed later this year.

BACKGROUND AND RATIONALE

Although submarines of the U.S. and other fleets are built to the highest technological standards, catastrophic incidents resulting in a breach of the pressure hull could result in the sinking of a submarine. In the event of such an accident survivors will face multiple challenges, including fire fighting, medical management of casualties, prevention of further fires and damage, rationing of water and food, and attempting to contact rescue forces. Current U.S. Navy disabled submarine (DISSUB) scenario models and contingency protocols contend with the potential contribution of toxic combustion byproducts to health decrement of survivors. These protocols provide guidance to the senior survivor in the event of a DISSUB incident and the toxic gas component of the protocol deals primarily with the major fire gases. These include carbon dioxide (CO_2), carbon monoxide (CO), hydrogen chloride (HCl), nitrogen oxides (NO_x), sulfure oxides (SO_x), ammonia (NH_3), chlorine (Cl_2), hydrogen cyanide (HCN), and hydrogen sulfide (H_2S).

Two action levels for each of the major fire gases have been recommended for incorporation into DISSUB survival protocols for introduction into the U.S. fleet (Table 2). Submarine Escape Action Level (SEAL) 1 is defined as the limit below which survivors can remain in the compartment without wearing respiratory protection for a maximum period of 10 days. If SEAL 1 is exceeded survivors will not utilize emergency air, but will plan to escape within 24 hours. At and above SEAL 2, survivors are required to use emergency air because unprotected exposure to the contaminant for less than 24 hours would likely result in significant impairment to respiratory and/or CNS function which would impair their ability to conduct an escape. If SEAL 2 is exceeded, the crew should initiate escape immediately. For each of the major fire gases, SEALs were recommended just below the threshold level for incapacitating effects reported in the literature that would prevent escape. The interactive effects of these gases have been described extensively in the literature (Table 1) and were also considered in assignment of SEALs (17-21).

Gases	**Interaction**	**Ref.**
CO+HCN	Synergism, additivity, or no effect?	18
$CO+CO_2$	Antagonism, additivity, or no effect?	18
$CO+SO_2$	Enhanced activity of SO2	17
$CO+\Delta T$	Enhanced by temperature above or below ambient	17
CO+HCl	Additive	20
CO_2 + other fire gases	Synergism	21
$HCN+NO_x$	Antagonism	21
Low O_2	Enhances toxicity of many fire gases	21
$HCN+H_2S$	Antagonism	19

Table 1. Potential interactive effects of major fire gases.

Until recently, studies of the interaction between the major fire gases have been limited to mixtures of only 2 to 3 gases. However, several models of the toxicological interaction of fire gases have been well described (20, 21). The role of combustion-derived particulate matter is also a major consideration in estimating toxicity.

The DISSUB scenario presents an extremely dynamic environment in which survivors must make a multitude of complex decisions. Lack of reliable and accurate portable detection technologies, the potential variability in compartment pressure and temperature, and multiple pulmonary injuries from fire and smoke inhalation are just a few of the additional factors which must be considered in developing a protocol to contend with toxic atmospheres in a DISSUB environment.

Gas	SEAL 1, 2 (ppm)	Comments	Ref.

CO	75, 85	• Goal to maintain 8.3% < [COHb] <12.4% because:
		  • 50% COHb generally considered lethal
		  • Nausea/vomiting at 15% COHb
		  • Effects on motivation and psychomotor ability <20% COHb
		  • Incapacitation at 30 min of 1000 ppm (<37% COHb)
		  • Potential interactive effects w/ HCN, CO2
			1,2,10
			1
			1
			2
			11

HCl	2.5, 25	• Based on immediate irritant effects on mucous membranes observed at >50 ppm • Tolerable up to 100 ppm • 60 min exposure to 10 ppm results in significant irritation • Because of humidity, will likely exist as an aqueous aerosol, resulting in some dermal exposure	3 3,4 3
HCN	1, 4.5	• Based on PEL of 4.5 ppm, 7-d SMAC of 1 ppm, IDLH of 50 ppm; CNS is target organ • Interaction between CO and HCN • Lack of dose-response data at low doses	7 5, 6
NO_x	0.5, 1	• Based on ocular and nasal irritation at 10 to 20 ppm • Induction of bronchitis or pneumonia at 25 to 75 ppm • 300 to 500 possibly fatal • Immunotox effects important following escape • Draeger tube available for NO2 only • Current ACGIH STEL = 5 ppm	8 7 7 8
SO_x	3, 6	• Based on bronchoconstriction, increase in airway resistance at >3 ppm for 120 h • Irritant gas in combination with asphyxiants and particulate; aerosol formation influenced by these factors	7, 11 9, 10
H_2S	10, 20	• Based on potential interaction with HCN • Pulmonary edema reported in prolonged exposures as low as 50 ppm • Ocular toxicity at 5 to 30 ppm	7 7, 12-14
Cl_2	2, 5	• NRC Committee on Toxicology guidance of 3 ppm for 60 min for submarine crews (1973 report) • Sig. Respiratory irritation in humans at 5 ppm • Eye irritation threshold at 7.7 ppm • Lethality at 40-60 ppm for <1 h	3 3 3
NH_3	25, 75	• Concentrations of ~25 ppm result in irritation • Severe pulmonary irritation at 100 ppm • Previous Navy report suggest 25 ppm is max limit for continuous exposure • Consider combined exposure to irritant gases	16 15 16

Table 2. Summary of Recommended SEALs.

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EFFECTS OF A PROLONGED SUBMARINE DEPLOYMENT ON SPECIAL OPERATIONS FORCES MISSION-RELATED PERFORMANCE

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Introduction

Physical exertion is intrinsic to many Special Operations Forces' (SOF) missions. Troops perform a variety of demanding tasks that require aerobic endurance, anaerobic bursts and physical strength. Physical demands of Sea-Air-Land (SEAL) operations may include swimming/diving, running, long load-bearing hikes, climbing, and piloting SEAL Delivery Vehicles (SDVs) (Prusaczyk et al., 1995). SOFs typically maintain intense physical training regimens to perform these tasks on real-world missions (Prusaczyk et al., 1991, 1994). Concern has been voiced that long transits with SOF units on board submarines results in a degradation of their mission-related performance. Factors that might contribute to poor mission-related performance are physical inactivity, alterations in exercise routines, changes in diet or sleep patterns, fluctuations of emotional or cognitive states, perturbations of submarine atmosphere and increases of medical ailments. Currently, it is uncertain that a decrement in performance exists and if it does, what impact any decrement has on operations. We conducted this field study to document decrements in mission-related performance and identify those factors that may have the largest influence on the identified decrements. A thorough description of the procedures and discussion of the results can be found in Sims et al., (1999) and Fothergill and Sims (2000). This paper highlights the main findings from these two reports.

Methods

Subjects

Subjects were recruited from SDV Team One and the USS Kamehameha SSN 642 in Pearl Harbor, Hawaii. Thirty-one subjects participated: 10 members in the deployed SEAL Team (DST), 9 members in the non-deployed SEAL team (NDST), and 12 members in the submariner control group (SCG). The average ages (± SD) of the DST, NDST and SCG were 29 (± 4), 30 (± 6), 28 (± 8) years, respectively. Data were collected on all three groups over a two-week period prior to the submarine deployment. The DST underwent a 33-day deployment then returned to Pearl Harbor from Korea by airplane and performed post-deployment tests. The NDST performed all "post-deployment" tests two days prior to the return of the DST. Post-deployment testing on the SCG was conducted once the submarine returned to Pearl Harbor following a total time of deployment of 53 days.

Pre-deployment and Post-deployment Measures

Cooper Test

Aerobic performance was assessed using the Cooper Test (Cooper, 1968). All subjects performed the test on the same outdoor track between 10:00 and 11:00 AM. Subjects ran around the track for 12 minutes attempting to reach the farthest distance possible. Both SEAL groups performed two pre-deployment runs each separated by one week. The first pre-deployment test enabled the SEALs to gain practice in pacing themselves to run maximally for 12 min. Unfortunately a busy pre-deployment work schedule permitted only one pre-deployment Cooper test for the SCG on the day before deployment. All subjects performed one run after their deployment period.

Physical Test Battery:

The physical test battery was designed by the Naval Medical Research Institute, in an effort to measure the basic skills and elements of physical conditioning thought to be important for SOF mission-related performance (Thomas *et al.*, 1994; Hyde *et al*, 1997). The battery consists of 1) Target Shooting 2) Hand Strength and Endurance 3) Manual Dexterity 4) Step Test 5) Pull-ups. These tests were performed in the order listed. All subjects, except SCG, completed at least two pre-deployment batteries each separated by one week. All subjects completed the battery after each group's respective deployment period.

Cognitive Test Battery

This cognitive test battery was designed by the Naval Medical Research Institute, in an effort to measure the basic elements of cognitive function thought to be important in SOF mission-related performance (Thomas and Schrot, 1995; Thomas *et al.*, 1995). The cognitive test battery is performed with the aid of a computer and consists of the following tests: 1) Matching-to-sample 2) Complex reaction time 3) Visual vigilance 4) Serial addition-subtraction 5) Logical reasoning 6) Repeated acquisition, in that order (see Thomas and Schrot, 1995). Performance on each test is determined by measuring reaction time and accuracy of responses.

Variables monitored throughout study period

Activity Levels

Activity levels were monitored with self-report logs. Subjects recorded daily activity on computerized bubble scoring logs. These logs were filled out for six days prior to deployment, three days at the beginning of deployment and for three days at the end of deployment. Subjects recorded time spent sleeping, working, exercising, eating and doing other activities in half-hour increments. Total time spent for each category, number of sleep periods and the longest single sleep period was calculated for each subject.

Mood States

Mood throughout the study was measured with a weekly 13 question Mood State questionnaire developed at the Naval Submarine Medical Research Laboratory.

Physical Health Symptoms

During the study all groups completed weekly health-symptoms questionnaires. This questionnaire was developed by Walter Reed Army Institute of Research for studying American troops deployed in Bosnia.

Submarine atmosphere

Submarine atmosphere composition was recorded every hour during deployment from the Central Atmosphere Monitoring System (CAMS-I) in three areas of the submarine: submariner berthing, Seal Team berthing and the Fan Room. Average partial pressures of oxygen, carbon dioxide, and carbon monoxide were calculated for each day for each location. When the CAMS-I system malfunctioned, oxygen and carbon dioxide levels were measured with a portable O_2/CO_2 gas analyzer. Gas measurements were not taken when the submarine ventilated with the outside or when the hatches were open while in port.

Data Analyses

For each individual, differences in performance between pre and post-deployment tests were calculated as a percent change from their pre-deployment test. These percent changes were then used to calculate the mean percentage change and ± 95% confidence limits for each Group. Planned comparisons between groups were conducted using independent *t*-tests, while paired *t*-tests were used to compare pre-deployment and post-deployment changes in the dependent variables. Sleep, exercise and mood data were analyzed using repeated measures analysis of variance. Pre-deployment frequency of reported subjective ailments were compared to deployment frequency using Chi-square. Statistical significance was set for all tests at $p \leq 0.05$.

Results

Physical and cognitive test batteries

The main decrements in the DST following deployment were in aerobic performance (Cooper test) and anaerobic performance (Step test) (see Table 1). Over the same time period the NDST showed no statistically significant changes in any of the physical measures. In contrast, the submariners showed significant improvements post deployment in Cooper test performance, step test performance and left hand grip strength. Shooting skills, manual dexterity, muscular strength and muscular endurance were unaffected by the 33 day deployment. We found no significant changes in any of the three groups between pre-deployment and post-deployment measures of time-to-completion or number of errors for matching-to-sample, complex reaction time, visual vigilance, logical reasoning, or repeated acquisition. We did find a significant slowing in post-deployment mean response time for serial addition-subtraction compared to pre-deployment. This slowing was seen for all three groups, SCG Mean ± SD (2232 ± 571 vs. 2040 ± 504 msec, respectively, $p<0.004$), DST (2049 ± 471 vs. 1807 ± 393 msec, respectively, $p<0.04$) and NDST (2170 ± 526vs. 1897 ± 502 msec, respectively, $p<0.06$). There was no change in errors for serial addition-subtraction for any of the three groups over the same testing period.

Activity Levels

For the NDST, there were no changes in time spent eating, working or recreating over the study period. Over the early deployment period the DST spent significantly more time eating and recreating and less time working than the SCG ($p<0.001$). For this same time period the DST had 66% more free time (recreational time) than the NDST ($p<0.001$). During the late deployment period there was no difference in hours spent eating and working between DST, SCG, and NDST. Over the study period no group significantly changed their amount of time spent exercising. However, the DST spent significantly less time exercising than the NDST over the entire study period, 0.7 vs. 2.5 hours/day, respectively ($p<0.01$). The SCG spent on average 1.5 hours exercising/day over the study period. There was no statistically significant difference between the DST and the SCG in time spent exercising ($p<0.07$).

Mood

There were no significant changes in any of the 13 mood measurements for the NDST over the study. However, for the DST, there were significant increases in feelings of annoyance, frustration, discouragement, depression, irritability, and tiredness ($p<0.05$). They also had a significant decrease in contentment, energy and activity levels ($p<0.05$). There were no changes

Table 1

Summary statistics for the change in performance following deployment on the different tests in the Physical Test battery for each subject group. * p<0.05 **p<0.01

Test	Pre-deployment Mean (SD)	Post-deployment Mean (SD)	% Change	95% Confidence limits
Cooper Test	Distance in meters			
Submariners	2317 (344)	2520 (279)	+10.1%**	+0.3% to +20%
DST	2839 (192)	2646 (242)	-6.8%*	-10.5% to –3.2%
NDST	2667 (187)	2730 (262)	+2.4%	-2.4% to +7.1%
Shooting	Number of hits			
Submariners	18.5 (4.8)	20.4 (3.6)	+18.2%	-6.3% to +42.7%
DST	29.5 (4.6)	26.4 (5.0)	-9.4%	-22.3% to +3.6%
NDST	22.1 (6.7)	22.2 (8.1)	+5.4%	-21.8% to +32.7%
Right Hand Grip Strength	Pounds			
Submariners	128.2 (18.4)	138.8 (21.6)	+9.4%	-0.9% to +19.6%
DST	127.7 (12.0)	127.1 (15.3)	-0.3%	-6.4% to +5.7%
NDST	129.0 (19.3)	123.9 (15.6)	-2.9%	-12.6% to +6.8%
Left Hand Grip Strength	Pounds			
Submariners	122.6 (22.9)	132.8 (24.4)	+8.7%**	+3.3% to +14.1%
DST	129.7 (12.0)	124.1 (16.9)	-4.3%	-11.0% to +2.4%
NDST	118.8 (15.9)	121.6 (20.8)	+2.9%	-8.4% to +14.1%
Endurance Right Hand Grip	Seconds			
Submariners	72.4 (22.7)	70.8 (19.1)	+7.9%	-25.6% to +41.4%
DST	66.9 (21.3)	61.8 (19.3)	-1.9%	-28.4% to +24.6%
NDST	72.8 (22.4)	69.7 (21.7)	-2.5%	-19.6% to +14.6%
Endurance Left Hand Grip	Seconds			
Submariners	67.8 (18.7)	54.8 (14.1)	-15.7%*	-31.9% to +0.5%
DST	63.3 (19.0)	65.2 (21.7)	+10.3%	-25.3% to +45.8%
NDST	75.9 (21.1)	72.7 (15.7)	-0.7%	-18.1% to +16.8%
Manual Dexterity[1]	Seconds			
Submariners	109.2 (30.6)	152.6 (69.9)	+38.1%*	+9.4% to +66.9%
DST	89.8 (16.4)	104.4 (28.4)	+17.4%	-3.8% to +38.7%
NDST	114.5 (41.1)	105.7 (31.9)	-3.9%	-22.7% to +14.9%
Step Test	Steps/minute			
Submariners	55.6 (6.5)	60.7 (7.4)	+9.2%**	+3.0% to +15.9%
DST	71.5 (7.3)	64.9 (8.4)	-9.2%**	-14.9% to -3.5%
NDST	66.8 (4.7)	67.0 (6.5)	+0.3%	-5.8% to +6.7%
Pull-ups	Counts			
Submariners	8.1 (4.6)	8.2 (4.3)	+7.5%	-12.1% to +27.1%
DST	17.3 (3.4)	17.0 (4.6)	-0.3%	-20.4% to +19.9%
NDST	17.9 (5.2)	19.0 (4.4)	+8.4%	-1.9% to +18.7%

[1] Note: An increase in time or positive change on this test is indicative of poorer performance. DST = Deployed SEALs, NDST = Non-deployed SEALs

in feelings of comfort, stress, nervousness, or tension. The SCG had no change in any of the above parameters except for an increase in energy during early deployment relative to all other periods ($p<0.05$) and a decrease in activity over the deployment ($p<0.003$). There were no differences in mood parameters between DST and NDST pre-deployment. However, the DST's mood in every category other than discomfort and nervousness was significantly worse than NDST during and after the deployment period ($p<0.05$).

Health

There were no changes in any of the 21 health symptoms reported by the SCG during patrol compared to prepatrol. For the NDST there was a decrease in muscle aches and rashes during the patrol period compared to prepatrol (both, $p<0.04$). During patrol, the DST had increases in the frequency of sinus troubles ($p<0.03$), headaches ($p<0.04$), constipation ($p<0.04$), and cuts/sores ($p<0.03$) compared to prepatrol. Whereas, the DST had lower complaints of muscle aches ($p<0.04$) during patrol compared to prepatrol.

Submarine Atmosphere

There was a total of 26 days of atmosphere data collected over the 33 days of SEAL Team deployment. Carbon monoxide levels never exceeded the limit of 15 ppm in any of the three locations over the deployment. The mean carbon monoxide level over the deployment was 1.65 ppm. Daily mean oxygen levels exceeded the upper limit of 160 mmHg for 3 of the 26 days (12%) but never fell below the 130 mmHg limit. The average oxygen level over the deployment was 145 mmHg. Daily mean carbon dioxide levels exceeded the limit of 3.8 mmHg for 9 of the 26 days (35%). The average carbon dioxide level over deployment was 3.5 mmHg

Discussion & Conclusions

In conclusion, a 33-day deployment on a converted ballistic-missile submarine resulted in statistically significant decreases in aerobic and anaerobic performance, and increases in medical complaints in members of this deployed SEAL Team. Some of the medical complaints may impact Dry Deck Shelter operations (e.g. increase in sinus problems). It is unknown to what level the observed degree of deconditioning will impact the SEALs performance during an actual mission; however, we hypothesize that mission-related performance would be most impacted when extended periods of physical exertion and short high intensity activity is required. It should be borne in mind that some of the observed decrements in performance of the DST may have been due to asynchrony of circadian rhythms and the effects of jet-lag resulting from their air flight travel from Korea to Hawaii immediately before conducting the post-deployment tests.

The significant improvements in aerobic and anaerobic performance of the SCG post-deployment is in marked contrast to previous studies in which significant decrements in physical fitness have been found in submariners following a prolonged deployment (Knight *et al.*, 1981; Bennett *et al.*, 1985). In the current study, practice effects will likely account for some of the SCG's improved performance after deployment since this group only performed the physical test battery once prior to deployment. Evidence of practice effects was indicated in the SEALs pre-deployment data which showed significant improvements in performance between the two pre-deployment tests for the Cooper test (+2% $p<0.05$) and the Step test (+12%, $p<0.0001$). An additional factor that may have contributed to the increase in post-deployment performance of the SCG is subject selection bias. Of note was the fact that several of the SCG were close to not meeting the U.S. Navy physical readiness standards. These subjects likely used the study as a means to motivate themselves to improve their fitness.

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DEVELOPMENT OF A BIOLOGICAL REACTOR FOR THE REMOVAL OF CARBON DIOXIDE FROM SUBMARINES

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Introduction

The most common technology employed to remove CO_2 from closed environments involves the use of 2-aminoethanol (MEA), a technology based on the formation of carbamino complexes. While MEA absorption of CO_2 is relatively efficient, the chemical is expensive and requires a significant amount of energy for regeneration. MEA in all forms is corrosive, toxic and volatile and forms ammonia upon decomposition thereby forming another toxic substance. Efforts to eliminate leakage of MEA from CO_2 scrubbers are not entirely effective and the long term health effects of exposure cannot be ignored. EnviroBio, in collaboration with Université Laval, has undertaken research and development to generate a bioreactor based on immobilized carbonic anhydrase for the removal of carbon dioxide from submarines. Carbonic anhydrase, an extremely stable monomeric globular zinc metalloenzyme of molecular mass 30,000 kD, has the highest molecular turnover number of any known enzyme. One molecule of carbonic anhydrase can hydrate 6 x 10^{7} molecules of CO_2 in 60 seconds [1,2]. Carbonic anhydrase catalyzes the following reaction:

$$CO_2 + H_2O \xrightarrow{\substack{\text{carbonic}\\ \text{anhydrase}}} HCO_3^- + H^+$$

Over the past several months, we have demonstrated that the concept of deploying an enzyme-based reactor to control and maintain physiologically acceptable CO_2 levels in submarines is technically feasible.

Enzyme immobilization

The bioreactor is a packed column with carbonic anhydrase immobilized onto the packing material. As reported elsewhere[3], the immobilization of an enzyme or other biocatalysts enables its repeated use. A packed column design has been adopted since it enables an optimal contact area between gas phase, liquid phase and solid phase (the packing material with immobilized enzymes). The first step in the development of such a bioreactor is the immobilization of carbonic anhydrase onto a suitable solid support.

The solid support adopted for our experimental bioreactor model is based on polymethylmetacrylate (PMMA), a polymer selected for its physical properties, chemical reactivity and microbial resistance. Carbonic anhydrase (CA) is attached to the surface of PMMA through a proprietary sequence of chemical reactions that results in a covalent bond between the enzyme and the solid support. Covalent linkage was selected because of its stability under various conditions.

The success of CA immobilization was evaluated by considering two characteristics (1) immobilized enzyme surface density (enzyme molecules/mm^2 of support surface) and (2) activity of immobilized enzymes per unit surface of solid support.

> **Protein assay:** Determination of the mass of enzyme immobilized onto the solid support was performed using two distinct methods: the bicinchoninic acid assay (Pierce) and an ELISA method. Briefly, the ELIZA technique consists first reacting CA with a monoclonal antibody "anti-CA II". In a second step, a second antibody (coupled to peroxidase) to anti-CA II is reacted after which the substrate o-phenylenediamine dihydrochloride (OPD) is added. The mass of immobilized CA is evaluated from the fraction of OPD transformed by the peroxidase.

> **CA activity:** The activity of immobilized CA is actually measured using a modification of the Wilbur and Anderson Assay[4]. This modification resides in the use of mechanical agitation to keep immobilized CA in suspension. The control is comprised of the solid support submitted to the immobilization protocol but without added enzyme; for free enzyme, the control consists of water only. With these modifications, the activity of immobilized and/or free enzymes was evaluated as described by Wilbur and Anderson[4] and is reported in units/mm^2 of support surface.
>
> Under such conditions, the activity of immobilized CA was evaluated under a CO_2 concentration of 40% (v/v), which is very different from CO_2 concentrations one would encounter in submarines. As well, assays were conducted in a Tris buffer solution whereas in the bioreactor pure water is likely to be used without any buffering species other than the bicarbonate generated by CO_2 transformation. Moreover, the enzymatic activity is measured at 1°C, which is colder than one would expect in the bioreactor. However, these conditions were used for ease of determination of immobilized CA activity. In pure water, the surface reactivity of the solid support under unbuffered conditions renders the evaluation of immobilized CA activity difficult because of the presence of interactions between the surface, water and the ionic species present (H^+ and HCO_3^-).

Two strategies have been explored for CA immobilization onto PMMA solid support: (1) immobilization onto an acidic PMMA solid support surface, and (2) immobilization onto an alkaline PMMA solid support surface. Acidic and alkaline surfaces were obtained following chemical treatments of the surface of PMMA after which different chemical reagents were utilized to covalently attach CA. For this purpose, 200 m PMMA beads were used (Polysciences). Work with such small beads enabled the determination of enzyme activity on small-scale equipment. Characteristics of best immobilization achieved with each strategy are reported in Table 1.

Table 1
Characteristics of immobilized enzymes onto PMMA solid support

Immobilization Method	Enzyme surface density (molecule/mm^2)	Activity (units/mm^2)
Acidic	8.0×10^{10}	0.2
Alkaline	1.3×10^{9}	1.7

From the results reported in Table 1 it can be observed that more enzyme molecules were attached on the acidic surface than on the alkaline surface. However, the activity per unit surface of solid support, which is the important parameter for the design of the bioreactor, was considerably higher for enzyme immobilized on the alkaline surface even though there was about 60 times less immobilized CA per unit surface. The reason for this observation most likely resides in the microenvironment of the bound enzyme-support interface. This is consistent with other reports detailing changes in the microenvironments of free and immobilized enzymes[5]. An acidic surface creates an acidic microenvironment for immobilized CA while an alkaline surface creates an alkaline microenvironment. Previous studies conducted in our laboratory indicate that free CA is more active, i.e. transforms more rapidly CO_2 in an alkaline environment. These results clearly demonstrate that CA immobilization on an alkaline surface is the strategy to be adopted for the construction of the bioreactor.

In order to evaluate the impact of immobilization on enzyme activity, the rate of CO_2 hydration obtained with immobilized CA (alkaline microenvironment) was compared with the rate obtained with free CA (no immobilization protocol). These rates were measured under the same experimental conditions (Wilbur & Anderson Assay). Table 2 reports activity for free and immobilized CA.

Table 2
Rate of CO_2 hydration for free and immobilized CA

Carbonic anhydrase	Rate of CO_2 hydration (mol/(L.s))
free	3×10^{-5}
immobilized	1.8×10^{-4}

Results reported in Table 2 indicate that CA immobilized on the alkaline PMMA surface transforms CO_2 faster than free enzyme. The reason for this important and significant 600% increase of enzyme activity most likely can be ascribed to the pH of the microenvironment at the site of immobilization and vindicates the decision to proceed with bioreactor design using an alkaline PMMA surface.

Enzyme Stability

Preliminary results indicate that free CA can be stored at 4 and 22 °C for 3 months without any decrease in activity. Similarly, preliminary results obtained with immobilized CA indicate that at 4°C enzyme activity remains stable for 2 months before any depreciable decrease in activity is noted. A longer-term more definitive stability study at 4, 22, 28 and 37°C comparing free and bound CA (immobilized under the optimum immobilization conditions described above) activities has been undertaken. Initial results indicate that immobilized CA activity remains unchanged at 4, 22 and 28°C after six weeks. However, at 37°C, a 60% decrease in immobilized CA activity was noted after six weeks.

Design of the bioreactor for a submarine

The next major step in this work has been directed to immobilization of CA to a PMMA support having the size and geometry suitable for a fully functional bioreactor. Some problems were encountered, i.e., commercial PMMA often contains additives that interfere with enzyme immobilization. However, "pure" commercial PMMA has been found and has been successfully utilized.

The main objective of the present research work is to design a bioreactor that will meet specific design criteria (Table 3). In this bioreactor, a gas containing CO_2 will enter the bioreactor and contact pure water that will absorb the CO_2 stream. Immobilized CA will transform dissolved CO_2 into H^+ and HCO_3^-. Overall, the CO_2 gas content will be reduced while H^+ and HCO_3^- will be eliminated in the outlet water. A schematic representation of the bioreactor is presented in Figure 1. Intellectual property associated with the use of CA in such a bioreactor has been protected and has "patent pending" status in several countries.

Table 3
Criteria for the design of the bioreactor

Parameter	Value
Crew size	60 persons
Total mission length	50 days
CO_2 concentration to be maintained	0.5% (v/v)
Available space	1.5 m^3

Prior to the design of a full-scale bioreactor, a laboratory-scale bioreactor must first be designed and constructed. The scale up of the bioreactor for a submarine will be performed using ChemCad software. Prior to the utilization of immobilized CA, the bioreactor will be operated using solely

PMMA solid support having a shape identical with that used to immobilize CA. This first step is required to bring final adjustment to the laboratory-scale unit and also to verify if ChemCad can accurately predict experimental results (if not, some adjustments will be implemented in the software). In a second step, the bioreactor will be operated with immobilized CA under various conditions close to those encountered in submarines. A kinetic study will also be performed. The kinetic model will be introduced into ChemCad and the theoretical results will be compared as before with experimental results. In cases where disparities are observed, some adjustments will be implemented in the ChemCad software once more. Once the software accurately represents experimental bioreactor performance, preliminary evaluations of dimensions, operating conditions and costs of a full-scale bioreactor will be performed.

In fact, the laboratory-scale bioreactor is operational. It has been operated with PMMA packing material without enzymes. Tests with immobilized enzymes will be conducted as soon as CA is immobilized onto PMMA packing material.

Figure 1: Schematic representation of the laboratory-scale EnviroBio Carbonic Anhydrase Bioreactor for removal of carbon dioxide.

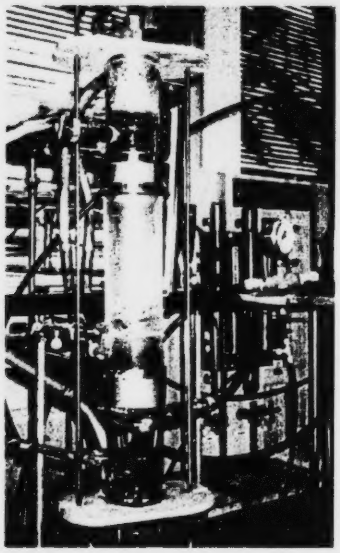

Fig. 1 Lab-scale bioreactor

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Assessment of Biofilter Technology for the Control of Trace Contaminants in Enclosed Environments

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Introduction

Biofiltration is an environmentally friendly technology that sees industrial application in the removal of contamination from process airflows. By utilising the metabolic processes of micro-organisms, contaminant species can be degraded to harmless products (essentially water, carbon dioxide and salts). On account of this, biofiltration constitutes a superior technique for controlling the organic contaminants present in submarine air, since the currently used carbon filters can only concentrate the contaminants for subsequent disposal on return from patrol. Other perceived advantages are the elimination of the fire hazard associated with saturated charcoal and a reduced maintenance requirement through not having to replace large amounts of carbon every time a boat returns from patrol. However, one very significant difference between the commercial and submarine applications is that, in the case of the former, biofilters are usually required to remove a single contaminant or simple mixture of contaminants at relatively high concentrations (100-10,000 vpm) whereas a submarine biofilter would need to degrade very complex mixtures (200-300 species) at low concentrations (typically 10vpm total). In consequence of this DERA Environmental Sciences has undertaken a programme of research to investigate the potential of biofiltration in submarine atmosphere remediation.

Laboratory-scale biofilter

Initial experiments were carried out at the laboratory scale using a biofilter constructed from two capped clear polyacrylic cylinders measuring 1.25m high by 0.3m id. Each chamber was filled to a depth of 1m with peat nodules and the upper plates were fitted with a water sprinkler system and outlet gas sampling lines. A centrifugal fan was employed to blow air through four-inch polypropylene pipe to the reactor chambers at a flowrate of 0.15 m^3/hour. Contaminant vapours were generated by bubbling air through Drechsel bottles containing the contaminant liquid. Adjustment of the air flow through the bottles enabled the quantity of organic vapour added to the biofilter inlet air stream to be controlled. In this way, VOCs could be presented to the biofilter at concentrations replicating those found in submarine atmospheres. Target concentrations were:

n-Octane	7.2 vpm
Toluene	2.4 vpm
n-Propanol	1.2 vpm
1,1,1-Trichloroethane	1.2 vpm

An inlet gas sampling line was fitted to the air supply pipe downstream from the point of contaminant addition. The concentrations of VOCs in the inlet and outlet air streams were determined by gas chromatography with flame ionisation detection (GC/FID).

The peat nodules were seeded with proprietary lyophilised cultures HAB1 and CX80 (Bord-na-Mona Ltd, Newbridge, Co.Kildare, Ireland) that had been reconstituted in nutrient broth containing 15 g/L Peptone and 5 g/L Yeast extract prior to inoculation.

Initial experiments demonstrated the basic feasibility of using biofiltration to remove trace organic contaminants. Following a 5 to 10 day period during which the microbial colony became established steady state removal rates of 100% n-propanol, 70% toluene and 20% n-octane were achieved over the ensuing 25-day period. No assimilation of 1,1,1-trichloroethane occurred, however this was not altogether unexpected as chlorinated hydrocarbons are notoriously resistant to bio-degradation, even in industrial applications. Other experiments undertaken with the laboratory biofilter were designed to investigate various parameters that might influence biofilter performance:

Nutrient supplementation Addition of a proprietary plant fertiliser (BabyBio™) to one of the two reactor chambers increased toluene and n-octane removal by an additional 30% and 15% (absolute), when compared to the control reactor.

Effect of humidity The optimum humidity was found to be 65-85%. Turning off the irrigation system, thereby effectively allowing the peat bed to dry out, demonstrated that the biofilter was capable of maintaining its performance for up to at least 20 days without water.

Incorporation of granular activated carbon (GAC) Evidence from the literature suggests that the incorporation of GAC into the peat matrix improves removal efficiency, particularly in circumstances where a biofilter is subjected to variable contaminant loads. This claim was investigated by layering one reactor with peat and GAC to produce a mixture containing 1.5% v/v GAC. Somewhat surprisingly, the performance of this bioreactor was inferior to the control. One explanation may be that uniform wetting of the peat was even more difficult to achieve with GAC incorporated.

Addition of surfactant Literature also suggests that the presence of low concentrations of surfactants can increase the soil-water mass transfer coefficients of organic pollutants, and therefore has the potential to increase biofilter performance. To investigate this, one reactor was washed with a solution of 30 mg/L Triton X-100™ before and after innoculation, and its performance compared with the control reactor which had been washed with the same volume of water. No improvement in performance was observed. In a separate experiment, it was demonstrated that the Triton X-100™ was being metabolised by the micro-organisms, and therefore the benefits of adding surfactants to a peat biofilter are doubtful.

Effect of washing It had been noted during earlier experiments that washing down the biofilter appeared to dramatically increase n-octane removal, although the effect was only transitory. Subsequent tests demonstrated that the phenomenon was reproducible and that addition of nutrient to the washing medium resulted in a greater increase than was achieved with de-ionised water alone. These observations can be explained by considering the growth kinetics of the micro-organisms. During the periods of high activity they are in the logarithmic phase of growth, but quickly move into the stationary phase followed by the phase of decline as the nutrients become expended. Washing removes dead cells and growth inhibiting waste-products which, combined with additional nutrient supply, restores logarithmic-phase activity.

Applied research technical demonstrator (ARTD)

Having proven the basic feasibility of using biofiltration to remove trace organic contaminants, an ARTD trial was undertaken to establish whether 'commercial off the shelf' (COTS) industrial technology could be scaled down for use on-board submarines. The 1/4-scale ARTD was purchased from Bord-na-Mona and was essentially a much smaller version of one of their industrial biofilters, comprising a biofiltration module with 2 m^3 filter bed volume. Air was drawn through the peat bed at a flowrate of 2 m^3/min using a centrifugal fan. A water sprinkler system was installed above the peat bed to maintain adequate moisture content. The air supply to the biofilter was dosed with controlled concentrations of VOCs using the same method as described for the laboratory-scale biofilter, and their concentrations in the inlet and outlet air streams determined using GC/FID. The filter bed was seeded with the same cultures and in the same manner as the laboratory-scale biofilter, but larger quantities were used.

Initially, steady state removal efficiencies of 100% n-propanol, 54% toluene, 35% n-octane and 30% 1,1,1-trichloroethane were achieved. However, following a period of further optimisation, which included reversing the direction of air flow, toluene and n-octane were removed with 100% and 54% efficiencies respectively. Performance of the ARTD was therefore shown to be capable of equalling that of the laboratory-scale biofilter, although it subsequently proved difficult to maintain it at that level. In order to assess whether a reduction in size of the biofilter could be achieved without sacrificing VOC removal efficiencies, the fan speed was increased by a factor of two, thereby halving the residence time. The overall effect, therefore, was equivalent to halving the size of the biofilter itself. As shown by the results below, this resulted in a significant loss of performance (Table 1).

Table 1
Performance of Peat Biofilter ARTD

Compound	Removal Efficiency(%)	
	60 sec Residence Time	30 sec Residence Time
n-Propanol	100	100
Toluene	100	61
n-Octane	53	32
1,1,1-Trichloroethane	39	28

After 11 months of continuous operation, the ARTD was shut-down pending maintenance of ancillary equipment and completion of the laboratory-scale experiments. As a final test, the biofilter was re-started 7 months later and, following the application of copious quantities of water, VOC removal efficiencies, comparable to those achieved earlier in the trial, were rapidly established. This result served to demonstrate the robustness of the peat biofilter. Unfortunately the requirement for a 1 second residence time rendered it far too large for the submarine application and the decision was taken that subsequent studies should focus on the biotrickling type of system.

Trials of the BIOVOX® biotrickling system

The washing experiments performed on the laboratory-scale biofilter, and experience with the ARTD, led to the conclusion that a biotrickling system, engineered to a high specification, would be much more efficient than the peat biofilter and therefore could possibly be made small enough to fit on a submarine. Following discussions with potential suppliers, the BIOVOX® system, manufactured by IBS-Viridian of Whitstable, Kent, UK was selected for trial. Important features of this system are that the biofilm is supported on a man-made substrate configured to give maximum surface area, and that the biofilm is continually washed with nutrient solution. The initial trial had the objective of determining whether VOCs could be removed with an efficiency at least as good as the peat biofilter, but within the much smaller footprint of the BIOVOX® system. Very encouraging results were obtained, i.e. 100% n-propanol, 90-100% toluene and 40% n-octane removal. Based on this data, and making judgements based on their experience in scaling-up for other industrial clients, IBS-Viridian estimated that a BIOVOX® volume of 11.5 m^3 would be required for biological treatment of submarine VOC contaminants.

Although this represented an almost four-fold improvement over the estimate based on the original peat biofilter, and despite its inherent advantages, a further reduction in size was deemed necessary before a BIOVOX® system could be considered for installation in a submarine. As a consequence of this, IBS-Viridian undertook further development and optimisation of their system, following which a second trial was undertaken. This was altogether more demanding since it presented the BIOVOX® with a much more complex mixture of VOCs (in excess of 100 species) more closely replicating the organic contaminant profile of a submarine atmosphere. Removal efficiencies for total VOCs and a selection of representative species are given in Table 2.

Table 2.
Performance of BIOVOX® Trickling Biofilter

Compound	Average Inlet Concentration (vpm)	Average Removal Efficiency (%)
Dichloromethane	0.13	42
1,1,1-Trichloroethane	0.16	27
n-Propanol	0.04	100
2-Butanone	0.08	100
n-Octane	0.18	73
n-Nonane	0.32	93
n-Decane	0.9	91
n-Undecane	1.1	65
Toluene	0.11	61
Ethyl benzene	≤0.01	39
m-/p-Xylene	0.04	71
m-/p-Ethyl toluene	0.08	58
1,2,4-Trimethyl benzene	0.17	79
Total VOCs	**23**	**59**

These results represent a significant improvement over those previously obtained since the airflow through the BIOVOX® system had been increased by 67% to 10 m^3/hr without loss of performance, thereby demonstrating the potential for a further reduction in size. Based on this new data, IBS-Viridian have estimated that a submarine BIOVOX®, operating at 1600 m^3/hr (the same flow rate as passes through a submarine main charcoal filter), would measure approximately 1.8 m x 1.8 m x 2 m (6.5 m^3 volume) in order to maintain total VOC contamination within the MPC_{90} of 10 vpm. This corresponds to a residence time of 15 seconds.

Conclusions

The basic feasibility of using biofiltration to remove trace organic contaminants present in submarine air has been demonstrated, however the size of peat biofilter required for the submarine application is likely to be prohibitive. Subsequent work has shown that a biotrickling filter (such as the BIOVOX® system) can achieve removal efficiencies of up to 100% when challenged with a complex mixture of trace level organic compounds, but within a much smaller footprint (estimated to be 6.5 m^3 volume). Although this represents a significant improvement over the peat biofilter, in comparison with the currently used charcoal filters (approximate volume 1.5 m^3) this may still be too large for the submarine application. Off-setting the size penalty, however, is the anticipated reduction in through life costs and the improved safety of a biofiltration system.

The size comparison becomes more favourable if a biofilter could perform more than one function. For example, if biofiltration can be shown to remove carbon monoxide and hydrogen concurrently with VOCs, then consideration could be given to replacing the high temperature catalytic burners in addition to the main charcoal filter (i.e. one item of new equipment for two old). Some studies addressing this issue have commenced, but are considered to be outside the scope of the present paper.

Acknowledgments

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Optimising the Air quality in Dutch Submarines[1]

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Abstract: The program for optimisation of the air quality in submarines of the Royal Netherlands Navy (RNLN) is based on two projects:

- The development of a new continuous method for the removal of carbon dioxide and
- the monitoring of the air quality in submarines on board during several months.

For carbon dioxide removal a new very promising regenerative system has been developed based on membrane gas absorption. Tests on a small-scale prototype have shown that the system is capable to remove carbon dioxide efficiently at concentrations between 0.5 and 1.5 %. Calculations show that the amount of chemicals used is far less compared to non-regenerative systems (e.g. based on Sofnolime).

To see the actual concentration of carbon dioxide and hydrocarbons on board, both were monitored for several months during a journey using a photoacoustic sensor. The measurements showed the influence of the charcoal filters, snorting and the carbon dioxide canisters.

Key words: Monitoring, Carbon dioxide, Activated Charcoal, Hydrocarbons and Membranes

Introduction: Air purification in Dutch submarines, which run on diesel fuel, is based on:

- the removal of hydrocarbons and other harmful gasses,
- the removal of particulate matter,
- the removal of carbon dioxide and
- the production of oxygen.

The present paper addresses only the removal of hydrocarbons and carbon dioxide.

The removal of carbon dioxide may be achieved by the use of non-regenerative absorbents like lithium hydroxide or Sofnolime. On-board regeneration of these absorbents is not possible. Although the use of the absorbents is simple and reliable, they are expensive and create a logistic burden. Especially during long trips the use of these absorbents is not practical because of the large quantity of adsorbent required. Besides the disadvantages of these non-regenerative techniques it is also the development of air independent propulsion (AIP.) for diesel-fuel submarines which urges a regenerative technique for carbon dioxide removal [1]. In this paper a new regenerative technique is described based on membrane gas absorption.

To obtain information for the design of the carbon dioxide removal, to study the adsorption behaviour of the charcoal filters in relation to the development of AIP and to get insight in the optimal changing rate of charcoal filters on board, a monitoring study was performed. A changing rate that is too high implies logistical consequences whereas a changing rate that is too low brings the risk of exposing employees to toxic concentrations of carbon dioxide or other compounds. In this paper a monitoring study is presented in which the carbon dioxide and the hydrocarbons concentrations were measured for several months.

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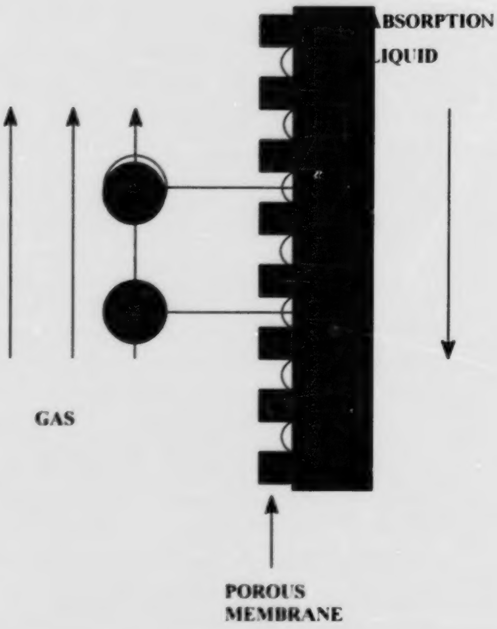
[1] The research was sponsored by the RNLN

Carbon dioxide removal



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The use of membrane gas absorption has been proven to be efficient for the removal carbon dioxide at concentrations between 0.5% and 1.5%. The method of carbon dioxide removal is illustrated in figure 1. A carbon dioxide rich air stream is brought into contact with an absorption liquid. The carbon dioxide rich-gas stream and the liquid are separated by means of a porous hydrophobic membrane. The porous nature of the membrane allows a rapid transfer of carbon dioxide to the absorption liquid. The hydrophobic character of the membrane prevents mixing of the air stream and the liquid [1]. The process is described schematically in figure 2. The carbon dioxide is removed from the absorption liquid by heating the liquid to its boiling point in a stripper. To prevent loss of absorption fluid the stripper contains a condenser. After the regeneration step the absorption fluid is transported back, through a heat-exchanger, to the cross-flow membrane unit (DAM module). The absorption liquid can be reused after the removal of carbon dioxide.

For the absorption of carbon dioxide TNO has developed a number of absorption liquids with a high affinity for carbon dioxide [2]. Compared to the state of the art-absorption liquid, e.g. aqueous solutions of monoethanolamine, the CO_2 Removal Absorption Liquid (CORAL) has several advantages: no membrane leakage, no loss of liquid due to evaporation, less corrosive and higher resistance to oxygen. To create an optimal contact between the CORAL and carbon dioxide a special cross-flow membrane unit (DAM) is used which enables a high mass-transfer of carbon dioxide [3]. After the CO_2 is desorbed the carbon dioxide will be transferred to the surrounding water by either injecting the carbon dioxide into the seawater or by mass transfer through a membrane.

The use of the apparatus in Dutch submarines requires a capacity 2.5 kg CO_2/hour to maintain a concentration of 0.5%. Naturally, it is possible to adapt the design to other capacities. This design has an estimated power consumption of 4.1 kW, including compression to inject the carbon dioxide into the seawater. Compared to a system based on LiOH canisters this is considerably higher. However further comparison with LiOH canisters shows that membrane gas absorption has the following advantages:

- Unlimited capacity, therefore no logistic burden
- In Dutch submarines a smaller volume is required for the membrane gas absorption equipment for journey where more than 217 LiOH canisters (approximately 120 hours) are taken along. Parts of the equipment can be built in as independent units, which simplifies the placement of the apparatus.
- Lower capital costs
- Reduced operational costs

Naturally, the use of Sofnolime and LiOH has already been proven in submarine conditions. This proof is not yet obtained for membrane gas absorption, however, several studies show that no major problems are to be expected.

Monitoring air quality:

During several months the air quality was monitored before and after a charcoal filter each eight minutes. Note that Sofnolime canisters were used to remove the carbon dioxide. The samples were drawn near the charcoal filter, which was situated in the men-quarters. It is expected that near the men-quarters the carbon dioxide concentration will be high. The

[redacted]

concentrations of saturated hydrocarbons and carbon dioxide were measured with a photo-acoustic monitor (Innova 1312) using a valve system (CBISS, C-DAS98). The Photo-acoustic sensor focussed on the saturated carbon - hydrogen bonds of hydrocarbons.

In figure 3 it is clearly visible that no gradual increase in the hydrocarbon concentration takes place during the sail. Obviously, the concentrations of both carbon dioxide and hydrocarbon vary mainly because of frequently snorting, mostly 3 times per day. The measurements did show to what extent the concentration will rise between snorting, which is valuable information for the development of AIP and the carbon dioxide removal method described above.

During the sail no difference in concentration was observed before and after the filter. This can probably be explained by the presence of large quantities of smaller hydrocarbons. These smaller hydrocarbons (e.g. methane) will not adsorbed on the charcoal however they add up during the measurement. The charcoal filters had been replaced just before sailing. It also seems that the charcoal filters did not reach saturation. The measurements will be continued next year, however to exclude the interfering of small hydrocarbon, an extra optical filter will be used aimed at aromatic hydrocarbons. During the sail no SMAC level was exceeded.

The carbon dioxide concentration was on average 0.2% during the sail. This low concentration can be explained as a result of frequent snorting as well as sailing above the surface after leaving and before arrival.

Conclusions

The membrane gas absorption apparatus developed by TNO is a very promising alternative to non-regenerative carbon dioxide removal. The technique will now be developed further to a fully operational prototype. Membrane gas absorption and an optimised changing frequency of the charcoal filters will reduce the logistical burden drastically. Monitoring of the air quality shows that the concentration hydrocarbons stays well below the SMAC level. However, the concentration hydrocarbons might possibly exceed this level by the introduction of AIP.

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A New Submarine Air Management System

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ABSTRACT

Modern submarines are designed for long time air independent missions. They are equipped with systems using new technologies e.g. fuel cells and also new materials for insulation as well as a host of electronic equipment. Several gases emitted by these systems can accumulate to unacceptably high concentrations in the submarine. Most of these substances could not be avoided without significant changes in submarine design or performance. For this reason there must be an absorption concept and system able to manage or collect harmful gases. Also, a gas detection and monitoring system is required to control the breathing air onboard the submarine.

To absorb carbon dioxide there are proven solutions already installed in submarines but no convenient system is available to absorb most of the other harmful gases released.

To offer a solution for an overall submarine air management system, Dräger commenced an R&D programme to develop an integrated system. The new system will consist of a carbon dioxide scrubber, a humidifier and a toxic gas absorber. On modern submarines the air condition causes a low relative humidity. Hence, absorption capacity of the soda lime is depending from the water content in the intake air. To improve the absorption capacity, a Humidifying section is installed upstream of the scrubber. Gas filters are placed parallel to the scrubber. The research phase is accomplished and a prototype is under construction presently.

For permanent control of submarine breathing air, a monitoring system based on IMS technology is available from Dräger now. This measurement technology can be adapted to different applications by selecting the gases that should be monitored. The performance is comparable with a GC-MS system but with less weight, power consumption and space requirement make this technology the better choice and appropriate for submarine air monitoring.

With these system components Dräger will soon be able to offer a complete solution for submarine air monitoring and purification.

Submarine Air Management and Monitoring System

In modern submarines designed for long duration air independent submerged missions, several gases generated by on board systems can accumulate to high concentrations in the submarine living areas. This is in addition to the gases and vapours emitted by its human occupants. Through a research and development program at Dräger, a solution is offered for an overall submarine air management system in order to manage, eliminate and/or collect these harmful gases. This system is also supplemented with an air monitoring system to control their concentrations.

The new system integrates the carbon dioxide scrubber, a humidifier and a toxic gas absorber (air purifier). In this paper, discussions are centred around the components that make up the new Submarine Air Management and Air Monitoring System. The Submarine Air Management System consists of three modules, namely the Carbon Dioxide Absorption Module, Humidifier Module and the Air Purification Module. These three modules are arranged in an optimum manner to provide an efficient submarine air management system. For permanent control of submarine breathing air, an Air Monitoring System based on the application of the principles of the ion mobility spectrometry is proposed.

Carbon Dioxide Absorption Module

The CO_2 absorption module is based on the existing A2000 non-regenerative system using soda lime as the CO_2 absorber. The construction of the A2000 is a stainless steel housing with a drawer type arrangement within which six soda lime cartridges are placed. Basic dimensions of the module are: 520mm L x 535mm W x 349mm H and it is designed for shock loads of up to 20 g in any direction. The A 2000 modules are of a fail-safe design and can be operated upon without tools. Due to its ergonomic design, there are no loose parts and time for cartridge exchange is minimised which is advantageous in comparison with existing scrubbers. Once installed with cartridges, the A2000 modules are maintenance free during a mission.
With the use of DraegerSorb® S, an absorption capacity of more than 125 Litre CO_2 /Litre sodalime is achieved at an ambient air temperature of 20°C and 60% relative humidity. The DraegerSorb® S is factory packed and sealed into plastic cartridges with dimensions 204mm L x 134mm W x 234mm H. Two openings (top & bottom) allow the flow of air through the soda lime bed when placed in the drawer of the A2000 module. Each cartridge has a total weight of 4.7 kg and contains 3.7 kg of calcium hydroxide granules shaped into hemispherical pellets of approximately 4mm diameter (Tyler Mesh 5-9) with water and sodium hydroxide as additives.

Fig 1. Absorption capacity of Draegersorb S w.r.t. temperature and humidity

The water content is 21%± 2% for optimum performance. The performance of Draegersorb® S in such a cartridge is shown graphically in Fig 1. The air flow is directed in parallel through the six cartridges in one A 2000 drawer.

The nominal flow rate through an A2000 module is 120 m^3/h. The pressure drop for the arrangement of the A 2000 scrubber including the set of cartridges is less than 600 Pa. If more modules of A2000 are required the modules can be arranged in parallel. The pressure drop will not be increased by this arrangement. A single A 2000 module is designed to absorb the carbon dioxide exhaled by 12 men at a CO_2 generation of 22 Litre per man per hour. Hence, for e.g. for a crew of 30, two modules of A 2000 are required.
During the research programme carried out by Dräger, relevant parameters and their influence on the performance of the soda lime was determined. One major result was that the flow rate is the decisive parameter. Also, the humidity in the ambient air should be at least at 60% at 20°C.

By installing an adequate number of A2000 modules, depending only on the number of crew in the submarine, a CO_2 level of the desired 0.5% by volume in the breathing environment within the submarine can be maintained. A maximum of three A2000 modules may be stacked on top of each other to form a composite module. Typical operating times are approximately 10 hours per cartridge set when the carbon dioxide level has to be maintained at 0.5% Vol. The A2000 module is shown in Fig 2.

Fig 2. A2000 Carbon Dioxide Absorption Module

Fig 3. Humidifier module

Humidifier Module

On modern submarines the air condition causes a low relative humidity due to efficient cooling. In certain instances, the relative humidity may fall below the minimum of 60% RH required for efficient CO_2 absorption. Absorption capacity of the soda lime is dependent upon the water content in the intake air. To improve the absorption capacity, a Humidifying module can be installed upstream of the CO_2 absorber thus improving the performance of the soda lime.

The humidifier module is designed along similar lines as the A2000 module retaining the housing/drawer concept and external dimensions. As such it can be integrated together with the other modules with ease. Humidifying of the air stream is achieved using the membrane principle. Water is supplied independently via a pump. The membrane elements are arranged in the drawer section of the module and are replaceable, the drawer arrangement allowing easy access to the membrane system for maintenance. This design is shown in Fig. 3.

The Humidifying of the ambient air is based on the membrane principle. A Polysulphone hollow fibre is fed with warm water on the outside of the fibre while the water vapour due to it's reduced partial pressure disappears through the membrane surface into the air stream passing by in the tube of the hollow fibre. Approx. 50 of theses fibres are arranged in a block glued at the end of the fibres to form a tight module. The patented modules have air inlet and outlet and water inlet and outlet adapters as well. The module's dimensions are 70 mm L and 45 mm W in a cylindrical shape. The performance of the membrane humidifier depends on the temperature of the warm water fed to the outside of the modules. A temperature of 60 °C is the minimum. Service life time of the modules depends on the purity of the water and distilled water is highly recommended as well as dust free air fed through the Humidifier. Particle filters in front of the module are recommended. The advantage compared with other membrane principles is that no additional power for heating is required. Warm water often is available onboard a submarine and on modern ships with fuel cells even distilled water will be available.

The membrane modules are arranged in a group of 32 per Humidifier module. The intake air is led through a particle filter matter into the membrane units that are connected with a water distribution block feeding warm water simultaneously into the 32 units. The Draeger Humidifier can also be used as an autonomous module due to a heating unit integrated in the 2 litre water tank. Thus the module can be retrofitted in existing submarines where no warm water is available.

The nominal flow rate is 120 m^3/h giving a humidity of up to 80 % RH at 20°C. Pressure drop of the module is below 1000 Pa and the power consumption is approx. 2 kW if the water must be heated by the integrated heating coil permanently from ambient temperature up to 60° C.

Air Purification Module

The air purification module is again designed as a housing/drawer arrangement with the same external dimensions to fit together with the other modules. Using another Draeger core technology, filter design, this module incorporates proven multi-gas filters in conjunction with particle filters and catalytic converters to improve the quality of the air within the submarine environment. This module operates in parallel to the CO_2 absorption/ humidifier modules.

The air is drawn in through a particle filter that retains and removes the heavier particulate matter before passing onto the gas filters & catalytic beds. Gaseous contaminants, for e.g. Ammonium & Formaldehyde are captured in the gas filter bed whose main ingredient is activated charcoal through absorption and adsorption processes. From here the air is directed to a parallel arrangement of catalytic beds, HT-Cat and AT-Cat. Carbon Monoxide is removed by the AT-Cat section which is uses a Palladium-Platinum-Catalyst operated at ambient temperature. Combustible substances such as Methane and Ethylene are removed at the HT-Cat section which is maintained at about 350°C. The HT-Cat consists of a special aluminium oxide in form of granules with a Palladium catalyst. An airflow of 100 m^3/hr is directed through this purification module and diverted at the catalytic beds. The quantity of carbon monoxide expected in the submarine air and its toxic effect leads to a major flow of 90 m^3/hr trough the AT catalyst. Only 10 % of the flow is led through the HAT-Cat. This is because Methane has no strong physiological effect on humans. Other combustible substances are not yet expected in high enough quantities to warrant removal. In this submarine air purification system only the HAT-Cat requires electric power of approx. 1 kW in addition to the power consumption of the blower unit. Pressure drop across the air purification module is approx. 1000 Pa.

Fig 4. shows this process in block diagram form. Exchange of filters and other maintenance is facilitated by the drawer type design. Fig 5. shows the design of this module as the housing/ drawer arrangement to fit together with the other modules.

Fig 4. Block diagram of air purification module

Fig. 5 Air Purification module

Air Management System arrangement

The Air Management System is a passive system in which the air stream is exposed to these modules by means of an externally installed blower and piping network. These three modules (Carbon Dioxide Absorption, Humidifying and Air Purification) are arranged vertically into an integral tower as shown in Fig 6. The Humidifying module is positioned at the bottom with the CO_2 absorption modules next up, followed by the Air Purification module on the top. The air flow is directed upwards through the tower passing initially through the Humidifying module and then through the CO_2 absorption modules.

Air Flow is directed to the Air Purification module in parallel to the airflow through the serial arrangement of the CO_2 absorber and humidifier.

Fig 6. Air Management System arranged as a tower

Air Monitoring System

Monitoring the air quality in the submarine living environment has been an important requirement for its sustained operation. Methods such as taking spot samples using detector tubes and using continuous monitoring instruments have been in use for some time now.

Ion mobility spectrometry (IMS) is a relatively new technology for detecting a large number of dangerous gases and offers real time quantitative and qualitative analysis. IMS offers a high sensitivity in the ppb to low ppm range. Combined with its high selectivity and fast response times, the IMS measurement system is an attractive extension of existing gas monitoring technology. It can be configured to monitor up to 8 different substances selectively. The IMS system developed by Draeger is free of vacuum or special gas system requirements and requires little or no sample preparation. It has a compact and rugged design and is built onto 19" rack mounts. Also, service and maintenance requires minimal effort. The performance is comparable with a GC-MS system but with less weight, power consumption and space requirement which make this technology an appropriate choice for submarine air monitoring.

Principle- IMS

The physical principle is based on the different drift velocities of positive and negative ions in a homogeneous electrical field at atmospheric pressure. The target gas is passed into an Ionization/ Reaction chamber in the IMS cell, where it is ionised by a Tritium source. Periodically ions are gated into a drift tube where the characteristic drift times, in an electric field, are measured. These drift times provide the basis for analysis as these identify the specific molecule ions and the current is proportional to the concentration of this compound. A microprocessor calculates the measured gas concentrations. Via analog interfaces the data is transferred to a controller (Draeger Regard) or a standard PLC. The results (compounds and concentration) are shown alphanumerically on a monitor with special evaluation software.

Through this technique, the online monitoring of the submarine environment and other important application fields for a wide range of gases is possible. Selected compounds for IMS are as follows:

Stark gases:	Cl_2, NH_3, HCN, NO_X, SO_2, HCl
Aldehydes:	Formaldehyde, Acetaldehyde
Halogens and Halogenated hydrocarbons:	J_2, Br_2, Cl_2, F_2, Methyl chloride, Chlorobenzene, Phosgene, (Chloromethyl)methylether, Dichlorethane, etc.
Isocyanides & precursors:	Toluene 2,4-diisocyanate, Toluene 2,4-diamine, Phosgene, Chlorine
Nitro compounds	DNT, TNT and other explosives
Chemical warfare agents:	Soman, Sarin, Tabun, VX, Mustard, N-Mustard, Lewisite, HCN
Aromatics:	Toluene, Xylene, Phenol, Aniline, Ethyl benzene
Solvents:	Acetone, Methanol, Ethanol, Phenol, Acrylonitrile, Dimethylether, Ethylacetate, Butylacetate
Microelectronics:	Diborane, Phosphine, Arsine
Bad smells:	H_2S, Mercaptans, Amines

Features

By using IMS, real time analysis is possible in the range of seconds which is favourable for online use. Processing can be carried out under normal conditions as no carrier gas is needed. The apparatus is compact, lightweight (6kg) and has a low power consumption (6W) which is suitable for mobile and stationary operation. Fig 7 shows in block diagram form, the components that build up the IMS instruments.

Fig 7. Block diagram of the components of an IMS instrument

Conclusion

Carbon Dioxide Absorption, Humidifying and Air Purification of the breathing air in the living compartments of a submarine is possible through the use of individual modules to manage each of these conditions arranged as a passive Air Management System.

Ion mobility spectrometry offers a real time quantitative and qualitative solution for monitoring the gases in living areas of the submarine.

With these system components Dräger will soon be able to offer a complete solution for submarine air monitoring and purification. The research phase is accomplished and a prototype is under construction presently.

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Feasibility of an Emergency Filtration System for Atmosphere Remediation in a Post-fire Scenario

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1. Introduction

Fires are a potential risk on all types of sea-going vessels and submarines are no exception in this respect. The fact that fires are an extremely rare occurrence on board the submarines in the British Royal Navy is due, in large, to the high level of manning aboard such vessels. Incidents with the potential to develop into fires do occur, but they are invariably detected by watchkeepers at an early stage and timely measures taken to prevent the fire developing.

With the increasing use of automated systems and centralised control and monitoring, the opportunity exists for reduced manning levels in future classes of submarines. This could well result in significant sections of a submarine, including the machinery spaces, being unoccupied for extended periods, apart from occasional watchkeeper inspections. The potential for incidents that could develop into a fire situation not being detected, would be significantly increased. Difficulties associated with effectiveness of automatic fire detection systems in the submarine environment, where considerable changes of humidity, temperature and atmospheric contamination by aerosols occur almost as a matter of course, mean that these systems may not provide a complete mitigation of this problem.

In the event of a fire aboard a submarine currently in service, the only remedial action available, if significant atmospheric contamination has occurred, is to either snort ventilate the boat or to surface. Such an action could be operationally undesirable, but the risk is accepted at the moment because of the infrequency of such incidents. For future classes where the risk may be higher, there would clearly be an operational advantage in being able to take remedial action after a fire without recourse to venting the boat externally.

With a view to providing this capability, we have been investigating the feasibility of developing an emergency filtration unit (EFU), which would be capable of removing contaminating gases and particulates from the atmosphere of a compartment, after a fire within has been extinguished. The unit would also be capable of replacing the oxygen consumed by the fire and would thus allow personnel to enter the compartment without breathing apparatus, after a suitable period of remediation. This should all be possible whilst the submarine remains at depth.

2. Post-fire Contamination

All fires are different. The species present and their concentrations in an enclosed atmosphere, after a fire has been extinguished, will depend very much on both what materials were burnt and what materials were pyrolysed by the heat of the fire without ignition. There are a wide range of materials present in a submarine, however, those present in the machinery spaces, (considered to be the spaces most at risk of fire), are largely materials such as fuel (diesel oil), lubricating oils, various plastic and rubber insulation materials, paints and laminates. The commonly encountered products of combustion from these materials are as shown in Table1.

Species encountered generally in high concentrations (10 – 10,000 vpm).	Carbon dioxide, carbon monoxide, hydrogen chloride, sulphur dioxide, oxides of nitrogen, hydrogen cyanide and organic compounds, such as benzene, toluene, styrene and acrolein.
Species encountered generally in low concentrations or as traces (< 10 vpm)	Hydrogen sulphide, ammonia, partially oxidised organic species such as formaldehyde, acetic acid and phenol.

Table 1
Typical Products of Combustion and Pyrolysis

A wide variety of compounds with varying properties are present in the atmosphere after a fire. Additionally, fires also generate quantities of smoke, soot and ash and the use of fire fighting agents such as Halons, can produce further contaminants, e.g., hydrogen bromide.

It would be very unlikely that one single process would remove all compounds having such a variety of properties to concentrations below the Maximum Permitted Concentrations for 24 hours of exposure (MPC24) or, preferably, below the level for 90 days exposure (MPC90), quoted in the British military standard BR 1326. This would be necessary for personnel to be able to enter an affected compartment without the need to wear breathing apparatus.

It was decided to adopt a modular approach to the development of an EFU, each module being designed to remove a group of contaminants with essentially similar properties. As different modules would employ different chemical processes, consideration had to be given to the order in which modules were assembled in the process flow. The ultimate objective would be to withdraw air from a fire affected compartment, treat it to remove contaminants and replace oxygen, then to return it, achieving an acceptable atmosphere within 3 to 4 hours of operation.

3. Laboratory Experiments

Laboratory experiments were devised, based on creating a simulated post fire atmosphere in a $0.75m^3$ sealed cabinet. 1 to 2 gram samples of typical materials found on submarines were burnt in the cabinet. This atmosphere was pumped at 10 to 20 litres/min through an apparatus to remove gaseous and particulate components, before being returned to the cabinet. The apparatus was developed by starting with a single removal stage and monitoring its performance, before adding further stages, (See Section 4 below). An increasing number of the contaminants were removed as each stage was added. The removal effectiveness of the apparatus with time and concentration changes in the cabinet were monitored throughout each experiment.

Experiments were repeated with several different materials. The materials chosen were butyl rubber, silicone rubber, PVC (unplasticised and foam) and polyurethane foam.

The flow rate through the apparatus was scaled to the anticipated flow through an EFU needed for a current RN SSN, assuming 90+% removal of contaminants at each pass. The objective was thus to reduce contaminant concentrations in the sealed cabinet to below MPC90 levels in 3 to 4 hours.

Gas analysis was carried out using Draeger tubes for most of the contaminants listed in Table 1. Total organic carbon based species were analysed collectively using a Foxboro TVA-1000A flame ionisation detector analyser, calibrated on methane and the oxygen concentration was monitored using a Draeger PAC IIIS electrochemical cell analyser.

4. Laboratory Apparatus Process Stages

The process stages used are given below, in the order in which they were added to the apparatus. The chosen order was that necessary to ensure that the processes at later stages would not be adversely affected by species not removed in earlier stages.

4.1 Aqueous Scrubber

For the laboratory apparatus, this was a cylindrical tower made of clear acrylic polymer, 720mm high and 78mm internal diameter. A 2 litre bed of 5mm dia. glass balls, was supported on a perforated plate in the tower. The process air was passed upwards through this bed whilst water, pumped at 1 litre/min from a 10 litre tank, was sprayed onto the top of the bed to trickle through. Some surface-active agent (0.005%) was added to the water to ensure wetting of the glass balls. The air was thus in contact with a large water surface covering the glass balls.

After materials were burnt, air was circulated from the sealed cabinet, through the tower and then returned. Gas analysis samples were taken before and after the tower.

It was found that the aqueous scrubbing process quantitatively removed the following species; Hydrogen chloride, hydrogen cyanide, sulphur dioxide, nitrogen dioxide and formaldehyde. Carbon dioxide, carbon monoxide, oxides of nitrogen (other than nitrogen dioxide), non-water soluble organic vapours, were not removed.

The process partially removed soot, however, the presence of particulates adversely affected the circulating blower. Therefore, a fibrous pad filter was placed immediately after the point of extraction from the cabinet, which removed all particulate matter.

An experiment was conducted with 2 % $^{w}/_{v}$ ferrous sulphate dissolved in the wash water. This achieved 30 to 50% reductions of the oxides of nitrogen concentration per pass through the tower. This was sufficient to obtain a reduction in contaminant concentration below the MPC90 (2.5 vpm) in the cabinet within 3 hours. The mechanism of this removal is the formation of a complex ion between the ferrous ion and nitric oxide, (which comprises the bulk of the oxides of nitrogen present).

Another advantage of the use of an aqueous scrubber as the first stage of a treatment process is the cooling effect achieved on hot process gas.

4.2 Catalytic Burner

This consisted of a 0.2 litre monolithic catalyst bed, connected to the outlet of the aqueous scrubber. The catalyst was of the precious metal platinum/palladium type and was introduced to oxidise carbon monoxide to carbon dioxide at ambient temperature.

In experiments, carbon monoxide was oxidised to carbon dioxide at room temperature with an efficiency above 90 %, when the inlet concentration was above 100 vpm. This reduced to about 70% when the inlet concentration fell to less than 20 vpm. This performance was sufficient to achieve a reduction of carbon monoxide concentration in the cabinet to below the MPC90 (15 vpm) in 3 hours of operation, despite a relative humidity of about 100 %.

In an unexpected development, the same catalyst, under the same conditions, effectively reduced oxides of nitrogen in the process flow when carbon monoxide was present;

e.g., for nitric oxide, $2CO + 2NO = 2CO_2 + N_2$

After the combustion of samples in the cabinet, the concentration of oxides of nitrogen was typically in the region of 25 to 50 vpm. Carbon monoxide concentrations were initially above 100 vpm and, as the reaction progressed, there was always sufficient present to achieve at least 40% removal of oxides of nitrogen. Thus, the reduction of oxides of nitrogen to concentrations of less than the MPC24 (5 vpm), and in many cases, to less than the MPC90 (2.5 vpm), was achievable within 4 hours of operation. This result provides an elegant alternative to the aqueous scrubbing with ferrous sulphate solution at Stage 1.

No loss of catalyst efficiency with time, e.g. due to poisoning, was observed.

4.3 Active Carbon Bed

The Foxboro TVA-1000 analyser showed that organic compounds were present in the process gas leaving the Catalytic Burner stage. The total organic carbon (TOC) concentration at this point at the start of an experiment was typically below 5 vpm, but there was a noticeable odour associated with the gas. Thus, a bed consisting of 0.2 litre of the broad-spectrum adsorbent, granular Sutcliffe Speakman 207C coconut shell based activated carbon, was inserted into the process flow.

Experiments showed that no detectable organic compounds were present in the process gas leaving the activated carbon and the gas was also odourless. The TOC analyser reading at the inlet to the apparatus (i.e. the concentration in the cabinet) was observed to fall to less than 1 vpm during the experiments. TOC readings at any point were never observed to exceed the MPC24 and MPC90 limit for total organic compounds, which is 10 vpm in both cases.

4.4 Carbon Dioxide Removal/Oxygen Production

Separate experiments on a different apparatus were conducted to investigate the means of removing carbon dioxide and replacing the oxygen consumed by combustion. The use of potassium superoxide was seen as a solution to this problem. This substance has the advantage that, in the presence of water vapour, it reacts with carbon dioxide and simultaneously produces oxygen, according to the following equations;

$$4KO_2 + 2H_2O = 4KOH + 3O_2$$
$$4KOH + 2CO_2 = 2K_2CO_3 + 2H_2O$$

This process has the potential to generate sufficient oxygen to raise the concentration in a fire affected compartment to above the original concentration before the fire, from the carbon dioxide present. In practice, it was found that the volume of oxygen produced by this process matched that of the carbon dioxide consumed.

Air at a relative humidity of over 80% and containing 1% by volume carbon dioxide was passed through a bed of granular potassium superoxide. Initially, all the carbon dioxide was removed and an oxygen concentration enhancement of 0.8% to 1% by volume achieved. As granules became coated in potassium carbonate, the carbon dioxide removal efficiency gradually fell to 70%, however, the oxygen production rate was consistently maintained.

A drawback of potassium superoxide is its oxidising nature and reactivity towards water. A large quantity (possibly 200kg) may be needed to treat a large compartment in a nuclear submarine. This would require a sealed containment, protected from water, contamination and heat, carried possibly for many years without use and yet, must be readily available when required. The problems of safe storage in a submarine have yet to be addressed.

An alternative, using established technology, would be to absorb the carbon dioxide into soda lime and carry oxygen in high pressure cylinders, or draw the gas from a LOX store, if a future submarine is equipped with an air independent propulsion (AIP) capability.

5. Envisaged Submarine EFU Equipment

The EFU equipment is likely to be contained either in a special compartment close to the highest fire risk areas, or in a fireproof sectioned-off space within the machinery spaces. Simple ventilation arrangements between the compartment to be treated and the EFU are required, however, a fire must not damage or destroy the EFU. Seal removal and damper operation needs to be as simple and rapid as possible and may need to be remotely operable.

The equipment is expected to consist of the process stages described in Section 4. It is currently estimated that such equipment would occupy approximately 4 to 6 cubic metres and weigh up to 1000 kg.

The aqueous scrubbing stage is likely to be of a matrix design with multi-angled spray nozzles, to allow for operation in a non-vertical attitude. The catalyst and packed particulate beds would be of a conventional spring-loaded design to resist shock and vibration.

6. Future Development

The next stage of the project will be to construct a quarter-scale technical demonstrator, based on the envisaged submarine applicable design, in collaboration with industry. This unit would be tested at a suitable facility, to carry out more realistic remediation simulations than was possible in the laboratory experiments. This would allow a more accurate assessment to be made of size, the identification of the potential for further size reduction and should also facilitate technical de-risking of the EFU.

Acknowledgements

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On board trials with a regenerative carbon dioxide scrubber

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BACKGROUND

Carbon dioxide removal based on CaO/CaOH or LiOH as the absorbing agents are commonly used in life support systems today. There is a need though for a simple, regenerative carbon dioxide scrubbing system for use in small confined spaces such as submarines and space stations. For this purpose Astrium GmbH (former Dornier, DaimlerChrysler Aerospace) has developed a scrubber system adsorbing CO_2 from the atmosphere by means of a weak ion exchange resin that can be regenerated by means of steam.

In 1998 a prototype scrubber of this kind was placed on board HSwMS Gotland, the first Swedish operational AIP submarine with Stirling auxillary machinery. The scrubber unit was located in the aft part of the Stirling room. A steam generator produced the water vapour for the regeneration process and the adsorbed carbon dioxide was dumped under the floor in the Stirling room. (The unit was designed for 3 men and did thus not contribute to the CO_2 elimination in the submarine.) The Defence Research Establishment was commissioned by Kockums Submarine Systems AB and The Swedish Defence Material Administration to supervise the function of the prototype scrubber.

SCRUBBER TECHNIQUE

The manufacturer has stated data presented in this chapter. The data originate from Product Information, Schauer & Kreis 1994, and internal DaimlerChrysler Dornier test reports (Test Report No.: RSBG-TR-8/95: Tests with a regenerative Carbon Dioxide Scrubber, September 12, 1995. Dornier internal report No.: TP-ECLS-DS-TN-024, Continuous Cyclic Tests.).

Scrubbing material

The scrubbing material is a specific highly porous weak basic ion exchange resin in bead form. The average bead diameter is between 0.8 to 1.3 mm. The overall external and internal surface of the resin is at least 50 m^2/g (BET). The polymer matrix material is functionalized with benzylamine groups in free base form. The functional group concentration is above 7.5 mol/kg. The manufacturer has successfully conducted more than 18.000 hours of operation with the material under laboratory conditions without indications that the materials lifetime should have been reached or even approached.

Adsorption procedure

The scrubber vessels are special containers filled with customised (according to the actual customer's requirements) quantities of the ion exchange resin beads. For scrubbing purposes CO_2 laden air is driven through the resin bed during the so-called adsorption phase. The carbon dioxide is getting adsorbed physico-chemically on the active groups of the resin material and purified air is leaving the bed until the resin reaches its saturation point. The theoretical capacity for carbon dioxide is at about 0.26 kg CO_2/kg resin (resin exposed to pure carbon dioxide for an unlimited period of time). In practice it is possible to reach about 20 to 25 % of its theoretical capacity for the conditions, which are commonly available in submarine atmospheres (in particular CO_2-levels at a maximum between 0.5 to 1 %. Should the CO_2 limits within a submarine be exceeded due to any reason, the scrubber is capable to reduce the level again down below the limits within a relatively short period of time.

Regeneration procedure

After saturation the resin is regenerated by applying hot steam, either at ambient pressure conditions and steam temperatures slightly above 100°C, or at reduced pressure levels, thus allowing lower temperature levels for the steam. CO_2 of a high purity (>95%) is leaving the resin bed during regeneration. This high purity makes it easy to further process/handle the CO_2. On a submarine, the CO_2 could be compressed in storage tanks, dissolved in seawater, or simply pumped overboard. After termination of the regeneration the resin can be used again for the next adsorption. Alternating desorption and adsorption can now follow.

Alternative regeneration methods are also possible, but these methods are leading to clearly lower concentrations of CO_2 in the regeneration exhaust stream, which will contain larger amounts of air. Further processing of the exhaust therefore would lead to the additional loss of air, for the application in confined manned volumes the steam method is obviously the most interesting one.

Power consumption

The regeneration is the power consuming part of the scrubbing process. An electrical power equivalent of less than 1.4 kWh/kg of scrubbed CO_2 was achieved under laboratory conditions, a further improvement is expected to be possible. Nevertheless it is necessary to use a large quantity of the capacity of the resin to achieve such low power consumption values, and, in addition, the thermal insulation effort in order to keep heat losses at a minimum is quite high. Both measures lead to the design of relatively spacious scrubber units. In order to save electrical power demand it is strongly recommended to use the availability of waste heat sources above a certain temperature level (> 60 to 70 °C) for the production of the steam. Under optimal conditions the use of waste heat sources on board of the submarine eliminates the request for electrical power demand.

The current co-operation between Astrium and Swedish navy/Kockums Submarine Systems AB focuses on a regenerative CO_2 scrubber system suitable to use the waste heat of the Swedish submarines AIP Stirling engine to produce sufficient amount of steam for the regeneration process. Carbon dioxide leaving the scrubber during the regeneration will be fed into the Stirling engine's exhaust gas, and thus will be withdrawn from the boat.

METHODS OF MEASUREMENT

On board measurements and sampling

The following parameters were continuously measured and recorded:

Parameter	Span	Sampling point	Type of sensor
Carbon dioxide (CO_2)	0-2 kPa	scrubber in and outlet	infrared
Oxygen (O_2)	0-21 kPa	scrubber outlet	electro chemical
Temperature (T)	0–100°C	scrubber outlet	Pt 100
Relative humidity (RH)	0-100 %	scrubber outlet	capacitive
Total pressure (*p*tot)	0-160 kPa		membrane

The following gases were intermittently measured using Draeger Chip Measurement System (CMS): Ammonia (NH_3), Carbon Monoxide (CO), Sulphur Dioxide (SO_2), Nitrous Fumes (NO_x), and Nitrogen Dioxide (NO_2).

Sampling for analysis of total volatile organic compounds (TVOC) was performed on solid adsorbent (tenax) followed by thermal desorption, GC separation and detection by mass selective detector. To characterise the content of volatile organic compounds in the submarine atmosphere the method of "Air profiles" has been used (Kristensson & Lunden, 1988).

Sampling for benzylamine analyses was performed using adsorbent tubes (XAD-2 tubes, two in series). Analysis was performed by Div. of Occupational and Environmental Medicine, Dep. of Health and Environment, Faculty of Health Sciences, Linköping University, Sweden using gas chromatographic technique (GC-NDP) (Ståhlbom, 1998).

The flow calibration curve made by the manufacturer was verified using an anemometer (GGA-75, Alnor, Sweden) and by volumetric measurements (G 1.6, Compagnie Des Compteurs).

Laboratory tests

Laboratory tests of the adsorbing material was performed by Div. of Occupational and Environmental Medicine, Dep. of Health and Environment, Faculty of Health Sciences, Linköping University and Swedish National Testing and Research Institute (SP) to study the behaviour of the material in overheating or fire.

Sampling for benzylamine analyses (impinger 0.1 M HCL, two in series) was performed when the resin was heated to 100-130°C in an oven. Samples were analysed using the same technique and equipment as for the on board samples.

To assess the potential fire hazard of the resin smoke generation tests and smoke gas toxicity analyses was performed by SP. The smoke generation tests were made according to ISO 5659-2, 1994. Three samples were exposed to an irradiation of 25 and 50 kW/m^2 each without any pilot flame and to 25 kW/m^2 in the presence of pilot flame. FTIR analysis (Fourier Transform Infrared Spectroscopy) was performed in one test at each condition to measure the concentration of CO, HCl, HBr, HF, HCN, NO_x and SO_2 as specified by the International Maritime Organisation (IMO, FTP Code Resolution MSC. 61(67), Chapter 1, Annex 1, Part 2). In one test condition (50 kW/m^2 without any pilot flame) gas analysis to determine the concentrations of volatile organic compounds (VOC) and benzylamine was performed using GC/MS.

Test protocol

The scrubber prototype has been in operation on board for a total of 446 hours during 15 occasions each lasting between 1 and 75 hours. During 66 hours while the submarine was moored to the quay the input concentrations of CO_2 was set at 0.2, 0.5, and 0.8 kPa (at nominal air flow) by addition of pure CO_2 to the air. Due to technical problems, and operational limitations while at sea, calculations of scrubber performance were made during the 66-h period when the input concentrations were controlled. Despite changing the packings it was found that the bed was leaking CO_2 during the regeneration process. This artefact resulted in a higher than normal CO_2 level at the beginning of the adsorption phase.

RESULTS AND DISCUSSION

On board measurements and sampling

During the on board trials the oxygen partial pressure range was 18 to 21 kPa. The carbon dioxide level ranged from 0 to 0.5 kPa and 96 % of the time the level did not exceeded 0.4 kPa. The temperature inside Stirling room ranged from 17 to 30 °C depending on season and the pressure (*p*tot) varied between 95 to 110 kPa.

Nominal air flow was according to the operation manual (Daimler-Benz Aerospace, Operation Manual, 1997) 37 kg/h. At 20°C this correspond to a flow of 32 m^3/h or about 530 l/min. Measurements after installation in the boat did not deviate more than about 3 % from the manufacturers flow calibration curve and Δp signals were thus used in calculations of the adsorption capacity.

Figure 1 illustrates one adsorption phase from one of the sea trials. Figure 2 originate from one of the tests at quay.

The addition of pure CO_2 was set to keep the inlet concentration at the desired level (0.2, 0.5, and 0.8) at nominal air flow (32 m³/h, minute 30-60). During the period with air flow below 32 m³/h (min 0 - 15) CO_2 was accumulated at the scrubber inlet and consecutively the CO_2 concentration at the scrubber inlet and the CO_2 adsorption was increased over the first part of the adsorption phase compared to normal operation at sea (see Figure 1 & 2).

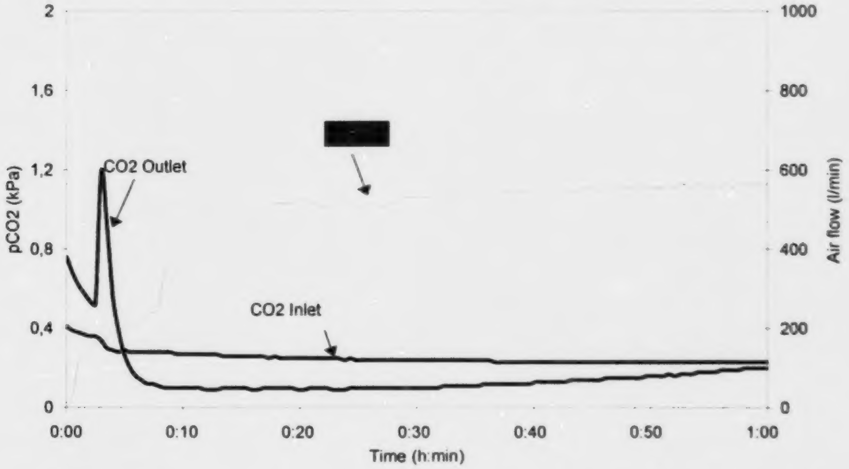

Figure 1. Example of one adsorption phase (60 minutes) from one of the sea trials. The outlet CO_2 concentration peak at the beginning of the adsorption phase originate from adsorbed CO_2 that remains in the scrubber bed after the desorption phase (20 minutes).

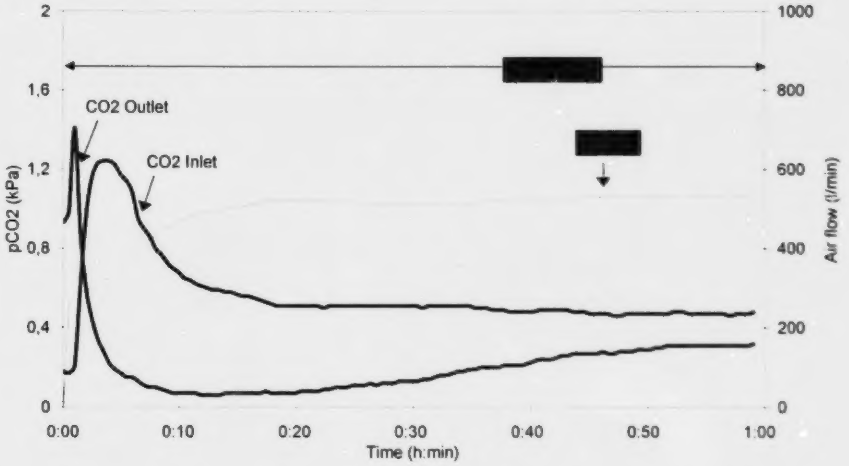

Figure 2. Example of one adsorption phase from the trials with inlet CO_2 concentration of 0.5 kPa. Minute 0-15 with air flow below 32 m³/h CO_2 was accumulated at the scrubber inlet and consecutively the CO_2 concentration at the scrubber inlet and the CO_2 adsorption was increased over the first part of the adsorption phase compared to normal operation at sea.

With a mean inlet concentration of about 0.25 and 0.6 kPa (minute 0-60) the adsorbing capacity was about 50 and 100 l CO_2/h respectively (0.29 and 0.54 l/min and man, see Table 1) which is according to the specifications. According to Det Norske Veritas (DNV, Rules for certification/classification of submersibles, 1988) and to limits set by the Swedish Occupational Safety and Health Administration (ASS) the volume fraction of CO_2 should not exceed 0.5 % at normal pressure (0.5 kPa).

Table 1. Mean and S.D. for scrubber inlet CO_2 levels and calculations of CO_2 elimination capacity. The scrubber was designed for 3 men (2.5-3 kg resin).

CO_2-inlet 30-60 min* kPa	CO_2-inlet 0-60 min kPa	CO_2 elimination 0-60 min l/min	Cycles # (n)
0.18 (0.01)	0.25 (0.13)	0.86 (0.13)	2
0.49 (0.01)	0.60 (0.02)	1.61 (0.01)	10
0.82 (0.03)	1.03 (0.01)	2.49 (0.03)	10

* at nominal air flow

Neither benzylamine nor NH_3, CO, SO_2, NO_x, or NO_2 were detected in air samples taken at the air outlet of the scrubber or in the ambient air around the scrubber. TVOC air profiles was in accordance with earlier analyses on submarine atmosphere.

Laboratory tests

Benzylamine was not detected when the resin was overheated or ignited. Aromatic hydrocarbons and nitrogen containing aromatic hydrocarbons were the dominant compounds in the smoke gases. CO, HCl, HBr, HF, HCN, NO_x and SO_2 did not exceed limits specified by the IMO. In all test-conditions the criteria for smoke values was exceeded (according to IMO). 1 out of 6 specimens ignited in the non-flaming exposure and in tests with flaming exposure all 3 specimens ignited. Smoke generation test at an irradiance of -50 kW/m^3 (non-flaming exposure) resulted in increased NH_3 production

CONCLUSIONS

Nothing has yet been found that would make scrubbers based on solid amine unsuitable for use on board submarines but the technical problems with the installation and the prototype used made it impossible to make conclusive tests. However:

- In a 46 h test the scrubber eliminated 0.54 l CO_2/man and minute at 0.6 kPa input.
- Benzylamine or other toxic gases have not been found during routine operation.
- At overheating NH_3 (ammonia) may be released. It is unknown to us how much or under what conditions. This should be investigated.

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PILOT PLANT PERFORMANCE OF AN AMINE REGENERATIVE SCRUBBER.

Effects of carbon dioxide loading, temperature and humidity during one thousand five hundred hours of scrubbing.

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Abstract

The Canadian Forces (CF) desire increased submerged endurance for the Victoria class submarines[1]. Extending the time between submerging and ventilating increases the demand on life support systems. Current soda lime based carbon dioxide removal systems have the capacity to remove the crew's metabolic carbon dioxide; however, the submarine does not have the space to hold enough soda lime to replenish the scrubbers over the entire mission.

One alternative is to use a carbon dioxide scrubbing material that can be regenerated with the addition of energy. The CF contracted Astrium GmbH Space Infrastructure to build a pilot plant regenerative scrubber based on their amine resin. The pilot plant was coupled with a steam plant developed under the same contract by Ballard Power systems. The CF wanted to validate the performance of the regenerative scrubber under closed-circuit conditions and over a longer period (1500 h). An environmental chamber at the Defence and Civil Institute of Environmental Medicine (DCIEM) was chosen as the site for the experiments. The study was designed to establish the carbon dioxide scrubbing capacity of the pilot plant and examine the effects of temperature and humidity on scrubber performance at the same time as testing the reliability of the scrubber over the 1500 h of operating time.

The pilot plant operated without failure for over 1500 h except for one temperature sensor failure in a secondary safety system. DCIEM staff corrected the problem through consultation with Astrium. During the experiments the capacity to adsorb carbon dioxide was found to match Astrium's design specification of 4 people and, through a factorial experiment, it was determined that the capacity was positively correlated to carbon dioxide loading and negatively correlated to temperature.

In summary, it appears that the amine resin is a mature technology. It could be used in a full-scale submarine scrubber for metabolic carbon dioxide removal given that enough energy and space are available; there is a suitable means of removal of the concentrated carbon dioxide; and that the heating, ventilation and air conditioning system adequately supplies the scrubber with carbon dioxide rich air and removes the water vapour added to the air by the steam regeneration.

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[1] formerly the Royal Navy Upholder class

Introduction

The Canadian Forces (CF) desire increased submerged endurance for the Victoria class submarines. Extending the time between submerging and ventilating increases the demand on life support systems. Current carbon dioxide removal systems based on soda lime have the capacity to remove the metabolic carbon dioxide production of the crew; however, the submarine does not have the space to hold enough soda lime to replenish the scrubbers over the entire mission.

Regenerative scrubbing systems eliminate this problem by recycling the scrubbing material. The regeneration process requires energy, a commodity in short supply when diesel-powered-electric submarines are running on their battery power. However, extending submerged time also means a change from the traditional diesel generator/battery storage system to atmosphere independent power systems. New power supplies bring possibilities for new efficiencies that will benefit atmosphere independent life support.

One possibility is the use of by-product heat from fuel generation for electricity-producing fuel cells. This waste heat can be used in regenerating the carbon dioxide scrubbers. Ballard Power Systems (Ballard), under contract to the CF, demonstrated this by connecting the methane reformer of a Ballard 50 kW proton exchange membrane fuel cell to a "solid amine" regenerative scrubber designed and built by Astrium GmbH Space Infrastructure (Astrium), formerly Daimler-Benz Aerospace Dornier. The scrubber was designed based on Astrium's experience with similar scrubbers built for the European space programme and pilot plants built for submarines [2]. The unit built to work with the Ballard methane reformer was designed to handle the metabolic carbon dioxide production of four people.

A steam plant formed the interface between the methane reformer and the scrubber. Hot oil collected heat from the methane reformer and this heat was used to produce the steam used to rejuvenate the Astrium amine adsorbent. Ballard commissioned and successfully tested the system for about 275 hours with one run lasting 168 h [1]. The experiments involved loading the scrubber with varying concentrations of carbon dioxide, but the tests were done under open circuit conditions. The results of the tests suggested that the scrubber could scrub twice the design capacity, i.e., eight people's carbon dioxide rather than four. Consequently, there was concern that the open-circuit tests were not representative of the true capacity of the scrubber.

The CF wanted to validate the performance of the regenerative scrubber under closed-circuit conditions and over a longer period (1500 h). To this end, the steam plant was also equipped with an electrically powered boiler that could feed the regenerative scrubber with the needed steam. An environmental chamber at the Defence and Civil Institute of Environmental Medicine (DCIEM) was chosen as the site for the experiments. The experiments were designed to establish the capacity of the scrubber and study the effects of temperature and humidity on scrubber performance at the same time as examining the reliability of the scrubber over the 1500 h of operating time.

Methods

The Scrubber

An electrically-powered steam generator was also built by Ballard to regenerate the scrubber independently of the fuel cell and methane reformer. The steam plant, Figure 1, was fed with power and fresh water and the output steam (2 Bar, 1.4 kg/h [1]) was fed to the regenerative scrubber. The scrubber was supplied with electrical power for the control circuits and the air blower and compressed air to drive the pneumatic valves used to control the flow through the two adsorbent beds, Bed #1 and #2.

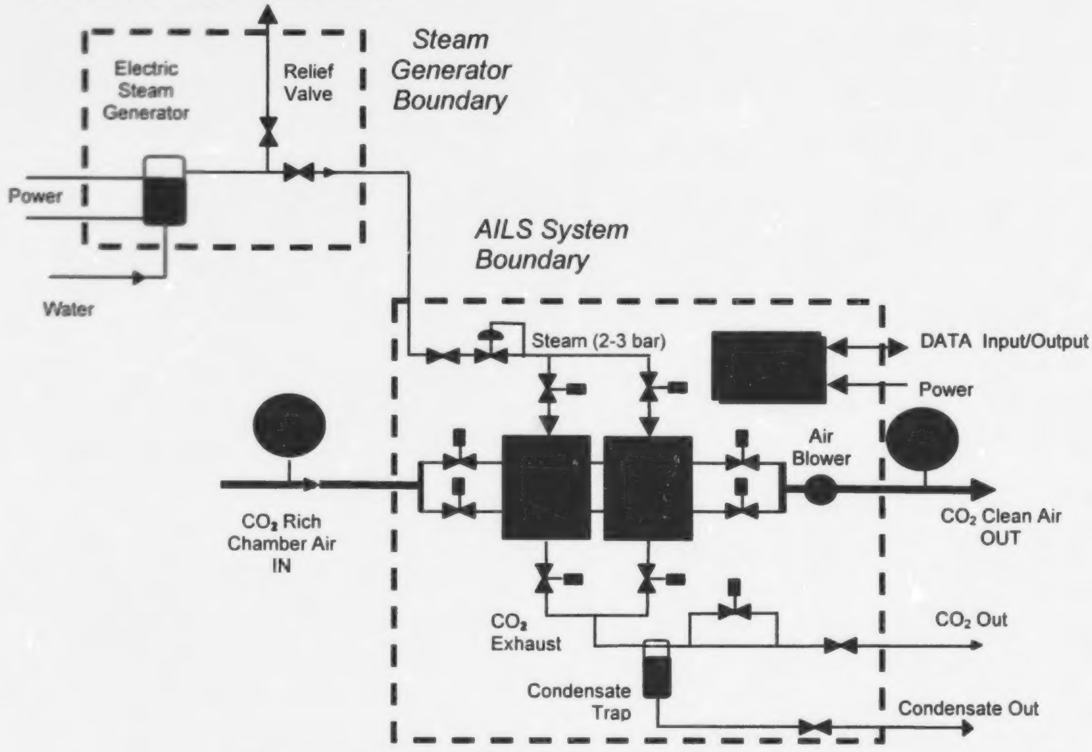
Electric Steam Generator
Relief Valve
Steam Generator Boundary
Power
Water
AILS System Boundary
Steam (2-3 bar)
DATA Input/Output
Power
Air Blower
CO_2 Rich Chamber Air IN
CO_2 Clean Air OUT
CO_2 Exhaust
CO_2 Out
Condensate Trap
Condensate Out

Figure 1. Regenerative scrubber and steam plant schematic. [1]

The adsorbent beds contained amine impregnated resin manufactured for Astrium to their specification, DOR-SA-028. The controller logic in the scrubber was such that the air blower drew carbon dioxide rich air through one adsorbent bed for purification. The purified air was blown out to the surroundings. The other adsorbent bed was sealed off and rinsed with steam to release the carbon dioxide from the resin. The carbon dioxide extracted from the resin by the steam regeneration was driven out of the bed by pressure difference. The scrubber's programmable control circuit timed the adsorption cycle and switched the resin beds from adsorbing to regenerating and back. Temperature sensors in the adsorbent beds shut the steam supply to the desorbing bed when the temperature in the bed rose to a pre-programmed level.

Set Up

The scrubber was installed in Environmental Chamber No. 4 (Foster Refrigeration of Canada, Model OUVT 34, volume ~74000 L) at DCIEM with the steam generator located immediately outside the chamber, Figure 2. The steam line, and all other pneumatic, water and electrical lines, penetrated the chamber wall through ports in the chamber that were subsequently insulated and sealed.

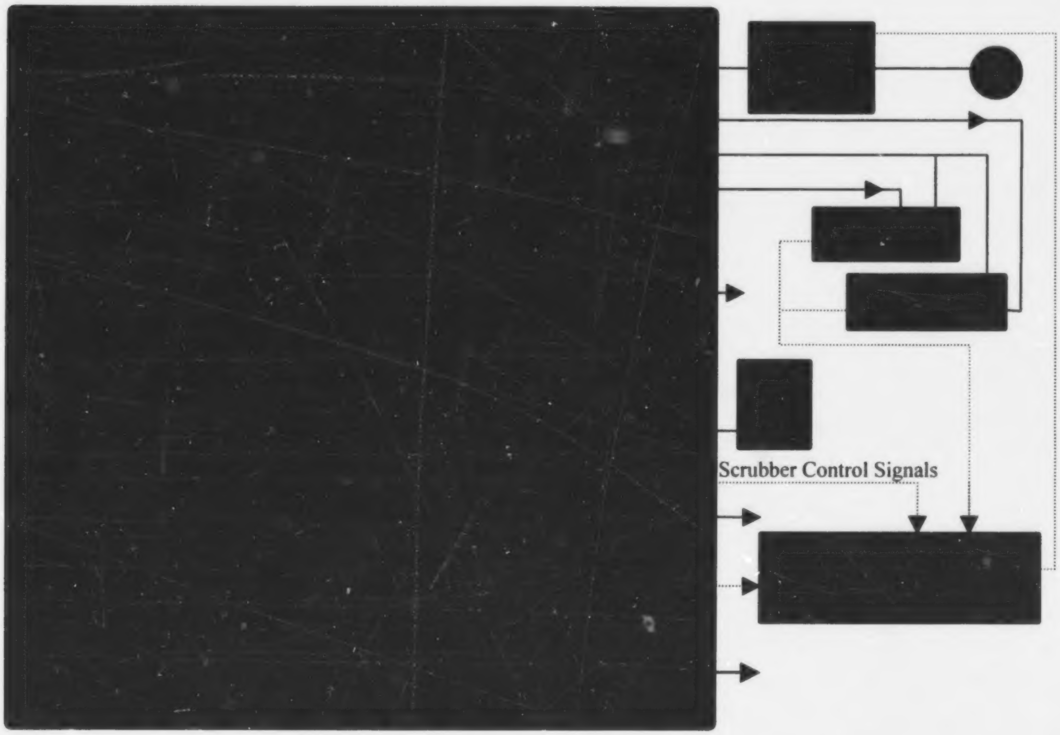

Figure 2. Experiment set up. Solid lines are fluids. Dashed lines are signals.

Carbon dioxide was injected into the centre of the environmental chamber from a compressed gas source via a mass flow controller (Brooks, Model 5850, 0-7 litres per minute ($L\bullet min^{-1}$) at standard temperature and pressure (STP) (0°C, 760 mmHg)).

Air from the scrubber exhaust and inlet was sampled continuously. The gas was dried using silica gel before analysis. Carbon dioxide analysis was done using infra red analysers (Analytical Development Company, Model PM3A-18821). Sample gas was returned to the chamber after analysis. Temperatures (Yellow Springs Instruments, Model 44004), and humidity (Vaisala, Humitter 50 U) at the inlet and outlet of the scrubber were also measured.

The carbon dioxide flow control and data collection were done using in-house written software using National Instruments LabView language and running under Microsoft Windows 95 on an Intel Pentium based personal computer. The software programmed a remote data acquisition system (Hewlett Packard HP 3852) to collect data and transmit it to the personal computer where it was stored and displayed.

The carbon dioxide driven off by the steam was collected in a chain-compensated gasometer (Warren E. Collins, 120 L capacity) for volume measurement. A sample of the collected gas was analysed for carbon dioxide content using a mass spectrometer (Perkin-Elmer, Model MGA 1100).

Circulation fans built into the environmental chamber kept the air in the chamber well mixed. Pilot studies showed no temperature or gas stratification in the chamber. However, the dehumidification plant in the chamber included an air refresh flow which amounted to a leak of carbon dioxide from the chamber. Consequently, two portable dehumidifiers were installed in the chamber with their drains directed to the outside of the chamber. A water lock was put in the hose to prevent chamber air exchange through the drain.

All feasible steps were taken to seal the chamber. Tests prior to the experiment showed the leakage rate to be about 0.06 $L\bullet min^{-1}$ of carbon dioxide at chamber carbon dioxide concentrations of 0.5% and 0.01 $L\bullet min^{-1}$ at concentrations of 0.1%.

Procedures

To begin the 1500 hours of testing the carbon dioxide injection rate was set to the equivalent of 2 people (One person's metabolic production was chosen to be 0.4 $L\bullet min^{-1}$ STP.), the chamber temperature was set to 20°C and relative humidity to 75%. The scrubber was operated at these conditions for seven days to obtain an understanding of the scrubber performance. At 20°C and 75% relative humidity, a step-wise optimisation procedure was used to balance carbon dioxide loading and capacity. The capacity was that carbon dioxide loading (to within 0.25 person's metabolic production) that resulted in an average chamber carbon dioxide concentration of 0.5%. After this, the effect of carbon dioxide loading, temperature and relative humidity were studied in a 2 level, factorial experiment with the levels as shown in Table 1.

Table 1. Factors and levels in factorial experiment.

Factor	Level	
	Low	High
CO_2 Flow (# of people)	1	*90% of capacity*
Temperature (°C)	10	30
Relative Humidity (%)	50	100

Procedures for running the experiments were simple. First the environmental chamber was activated and set to the desired temperature. The humidifiers were turned on or off depending on the humidity desired. The steam plant was activated and allowed to reach operating temperature and pressure. The scrubber was turned on, all carbon dioxide analysers were calibrated (spanned against a primary standard of 1.00% carbon dioxide in air, and zeroed against pre-purified nitrogen) and then the carbon dioxide injection was started. The scrubber was left to run until it failed or until the end of the 1500 h. Carbon dioxide analysers were calibrated at least once every 24 h and sample gas desiccant was replaced when indicated by desiccant colour change. The scubber was left running while temperature, humidity or carbon dioxide loading were changed and the conditions were allowed to stabalize.

Results

Operation Over 1500 h

The reliability test exceeded the 1500 h goal. A total of 1497.2 h were completed during the experiment and it operated for more than 5 hours during the commissioning of the scrubber.

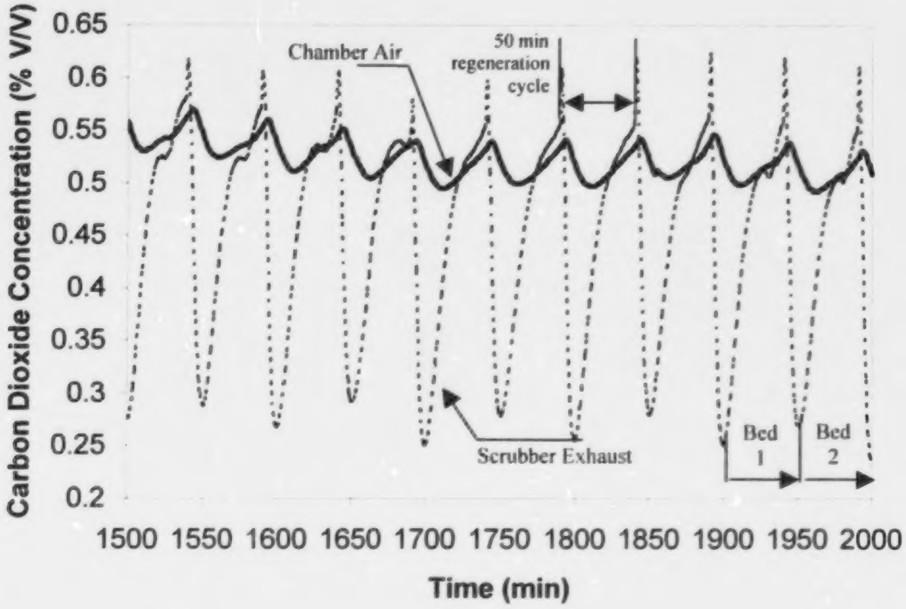

Figure 3. Sample of carbon dioxide concentrations in regenerative scrubber exhaust and chamber air during 500 minutes on March 21, 2000. Carbon dioxide loading was 1.4 L•min^{-1} (3.5 persons). Chamber temperature was 20°C and relative humidity was 75%. The maxima and minima clearly show the 50 minute adsorption cycle. The carbon dioxide spike in the scrubber exhaust at the start of the adsorption cycle resulted from a clearing of the concentrated carbon dioxide in the regenerated bed. The scrubber exhaust minima show an interesting difference in the performance of Bed #1 and Bed #2.

Throughout the trial, the carbon dioxide levels in the chamber and in the scrubber exhaust followed predictable patterns, Figure 3. This shows the cyclic pattern of carbon dioxide in the scrubber exhaust and chamber air. Both levels followed a 50 minute cycle with the switching of the air flow through the two adsorbent beds.

At the beginning of the 50 minute adsorption cycle, the scrubber controller would switch from the spent bed to the regenerated bed. The switch would produce a momentary spike of the remaining concentrated carbon dioxide purged from the regenerated bed. The exhaust carbon dioxide quickly dropped as the left over carbon dioxide was cleared. Interestingly, the minimum concentration for Bed 1 tended to be slightly lower than Bed 2. This was traced to less exposure to steam in Bed 2 believed to be related to a lower threshold temperature for Bed 2.

Over the adsorption cycle, the exhaust concentration and the chamber concentration of carbon dioxide increased. The exhaust concentration eventually matched the chamber concentration. (It appears in Figure 3 that the exhaust concentration sometimes exceeded the chamber concentration, but the overshoot was a result of calibration differences in the two infrared analysers.)

During the adsorption cycle the other amine bed was being regenerated with steam. The steam regeneration ended when the temperature of the regenerating bed reached a programmed threshold (about 90°C). Steam regeneration took about 30 minutes with the chamber temperature at 20°C. The bed regenerated was ready to start adsorbing when the next 50-minute cycle started.

Failures during the 1500 h trial were marked by interruptions to the standard pattern. In the first week of testing the scrubber failed to regenerate for 3 adsorption cycles because of a power interruption to the steam plant. Once the steam plant was reactivated, the scrubber returned to its regular scrubbing pattern. During the first weekend of the test period the scrubber needed to be shut down owing to a scheduled weekend power shutdown to the building main power. The only true failure of the scrubber came 4 days after the weekend power shutdown. An investigation of the problem identified a failed temperature sensor in a secondary safety system. It was indicating that the temperature in Bed #2 was exceeding a safety limit. Consequently, the control logic never turned the steam on to regenerate the bed. After a day of testing and electronic mail consulting with Astrium, the sensor was eliminated from the circuit. From then on the scrubber and steam plant operated for 1272 h (53 days) without failure. However, there was a four day shut down owing to staff unavailability and a 20 minute shutdown to install measuring leads on the failed temperature sensor. The longest continuous period of operation was the 36.8 days prior to the end the test.

Carbon Dioxide Adsorption Capacity

The carbon dioxide adsorption capacity of the scrubber was first determined to be equivalent to 3.5 persons over two separate trials, Table 2. The iterations started at a metabolic carbon dioxide load equivalent to 2 people which produced an average carbon dioxide concentration of about 0.15%. The carbon dioxide injection rate was increased to 4 people. This forced chamber CO_2 concentrations above 0.5% so the next iteration was set to 3 people. This was too low. The load was increased to 3.5 people and the average chamber concentration was 0.50% for a period of 17h after a stabilisation period of 27 h. The iterations continued by increasing the load to 3.75 people. This proved too much so the load of 3.5 people was repeated. After stabilising for 47 h, the chamber carbon dioxide concentration averaged 0.46% for the 22 h remaining in the test.

When factoring in the leakage rate of 0.06 L•min^{-1} the carbon dioxide load would be reduced to the equivalent of 3.35 people. This was lower than the 4 people predicted by Astrium. When examining the data it became clear that the scrubber was not adsorbing as much carbon dioxide as possible. The adsorption cycle was 50 minutes but the regenerating bed was only steamed for about 30 minutes before it was ready to start adsorbing again. On the other hand, the adsorbing bed was nearly saturated after 30 to 35 minutes so very little carbon dioxide could be adsorbed. It seemed possible to reduce the adsorption cycle time and increase the adsorption capacity. Astrium agreed and provided a software change to reduce the adsorption cycle time to 40 min.

***Table 2.** Effect of carbon dioxide load on chamber carbon dioxide concentration for 50 minute scrubber regeneration cycle.*

TEST	CO_2 LOAD (PERSONS (L•MIN^{-1} @STP))	AVERAGE CHAMBER CO_2 CONCENTRATION (% V/V)	RANGE OF CHAMBER CO_2 CONCENTRATION: MIN:MAX (% V/V)
1	2 (0.8)	0.15	0.13 : 0.18
2	4 (1.6)	0.60*	-
3	3 (1.2)	0.40	0.34 : 0.44
4	**3.5 (1.4)**	**0.50**	**0.47 : 0.55**
5	3.75 (1.5)	0.61	0.54 : 0.67
6	**3.5 (1.4)**	**0.46**	**0.42 : 0.51**

- *Test was terminated after 20 hours of continuous rise in chamber carbon dioxide concentration. There was no sign of the carbon dioxide concentration reaching equilibrium
- **Bold text** indicates test with a balance between loading and adsorption.

The scrubber logic controller was reprogrammed with the new software and the step-wise optimisation was repeated. The best balance between loading and adsorption capacity was achieved with a load equivalent to 4 people, Table 3. When taking into account the chamber leakage rate at 0.5%, the metabolic rate would be equivalent to 3.85 people (1.54 L•min^{-1}). In hindsight it would have been interesting to increase the load by the leakage amount to see the effect on chamber carbon dioxide concentration.

***Table 3.** Effect of carbon dioxide load on chamber carbon dioxide concentration for 40 minute scrubber regeneration cycle.*

TEST	CO_2 LOAD (PERSONS (L•MIN^{-1} @STP))	AVERAGE CHAMBER CO_2 CONCENTRATION (% V/V)	RANGE OF CHAMBER CO_2 CONCENTRATION: MIN:MAX (% V/V)
1	**4 (1.6)**	**0.48**	**0.39 : 0.54**
2	5 (2.0)	0.63	0.61 : 0.71
3	4.5 (1.8)	0.56	0.52 : 0.61

- **Bold text** indicates test with balance between loading and adsorption.

The load versus capacity balance was also studied using the gasometer volume measurements and analysis of the gas collected from the scrubber regeneration process. These data were analyzed to determine the amount of carbon dioxide adsorbed and released by the scrubber. The average carbon dioxide concentration of the ejected gas was 95.7% for Bed #1 and 97.5%

for Bed #2. When normalised to standard temperature and pressure, the carbon dioxide volume extracted from Bed 1 was 68.9 ± 9.39 L, n=23, and from Bed 2 was 70.9 ± 8.13 L, n=18. The difference between the two beds was not significantly different ($p>0.05$, Student's t, two-tailed).

These values compared favourably with the amount of carbon dioxide added to the system during the 50 minute cycle when the chamber carbon dioxide concentration was balanced at 0.5%, i.e., the amount extracted was the same as the 70 L (3.5 person load) added, Table 4. When the cycle time was reduced to 40 minutes the correlation was not as clear. The amount collected in the gasometer was higher than the 4 person load used to reach 0.5% equilibrium. The collected amount was closer to a 4.25 or 4.5 person load. Accounting for the leakage rate would drop the allowable load to between 4.1 and 4.35 people. This is higher than the 3.85 people established from the chamber carbon dioxide concentration but still close to the 4 person design specification used by Astrium.

Table 4. *Volumes of carbon dioxide injected during 50 minute and 40 minute regeneration cycles for increasing metabolic loads.*

INJECTION RATE		VOLUME (L @ STP)	
People	***L•min^{-1} @ STP***	***50 minute cycle***	***40 minute cycle***
1	0.4	20	-
2	0.8	40	-
3	1.2	60	-
3.5	**1.4**	**70**	-
3.75	1.5	75	-
4	1.6	80	64
4.25	**1.7**	-	**68**
4.5	**1.8**	-	**72**
5	2	-	80

- Bold text indicates test with balance between loading and adsorption.

Factorial Experiment

The conditions tested in the factorial experiment are listed in Table 5. Carbon dioxide flow and temperature were regulated closely (temperatures within ±0.5°C and carbon dioxide injection rates within ±0.05 L•min^{-1}). However, the humidity control was poor. The dehumidifiers managed to achieve "Low" humidities between 54% and 76% and "High" humidities between 84% and 85%. Consequently, without a large difference in relative humidity the analysis was not sensitive to effects of relative humidity.

The carbon dioxide injection rate did significantly affect the chamber carbon dioxide concentration (ANOVA, $p=0.05$) as would be expected. The influence of temperature was only significant at the $p = 0.1$ level under analysis of variance. A stronger relationship was expected because heat drives the carbon dioxide from the amine. Astrium recommends operating the scrubber with inlet temperatures lower than about 25°C. Additionally, further evidence that there was a strong relationship between inlet temperature and carbon dioxide scrubbing capacity came when the chamber refrigeration system shut down over the weekend, Figure 4.

Table 5*. Regenerative Scrubber Factorial Experiment Design*

Test	CO_2 Flow (L•min^{-1} @STP)	Temperature (°C)	Relative Humidity
1	0.4	10	Low (50%)
2	1.26	10	Low (50%)
3	0.4	30	Low (50%)
4	1.26	30	Low (50%)
5	0.4	10	High (100%)
6	1.26	10	High (100%)
7	0.4	30	High (100%)
8	1.26	30	High (100%)

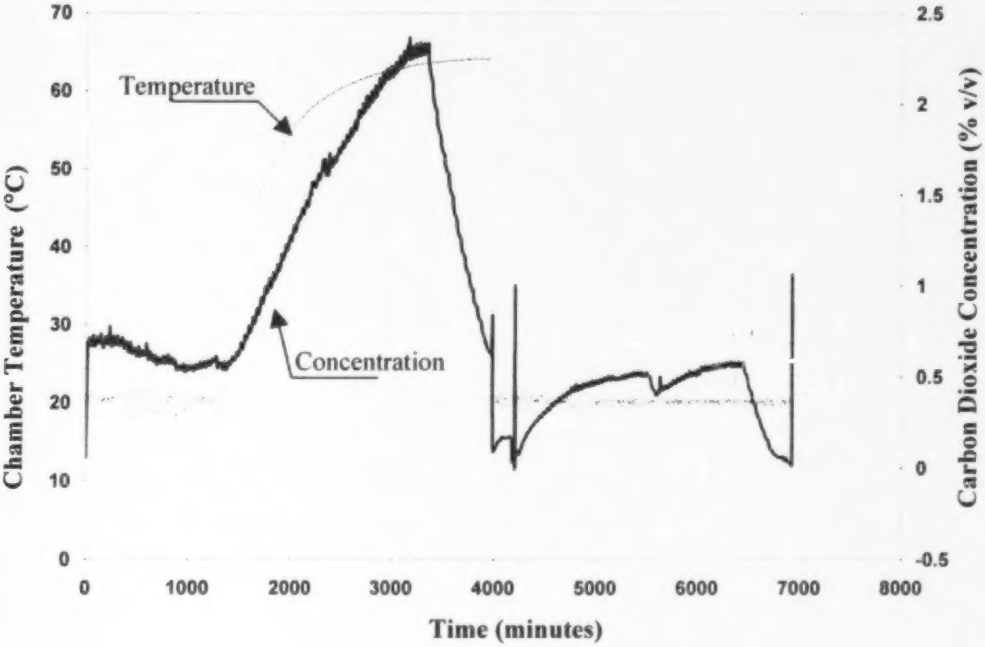

Figure 4*. Effect of temperature on scrubber capacity during an episode where the chamber refrigeration system failed over a weekend. The scrubber continued to cycle; however, the amine temperature increased and its adsorption capacity subsequently dropped and the chamber carbon dioxide concentration increased. The chamber carbon dioxide concentration began to drop (3400 min) when the problem was discovered and action was taken to turn off the carbon dioxide injection flow. After the chamber refrigeration system was repaired and the chamber temperature restored to 20°C, the scrubber continued to operate normally. The sharp spikes in the concentration are calibration points.*

With the failure of the refrigeration unit, the temperature rose to greater than 60°C and the carbon dioxide concentration in the chamber increased with the temperature. The concentration continued to rise until the problem was detected and the carbon dioxide injection was shut off. Once the refrigeration unit was reset and reactivated, the chamber temperature returned to 20°C, the carbon dioixde injection was reactivated and the carbon dioxide concentration returned to the 0.5% equilibrium level.

Other Analyses

In addition to the effects on chamber carbon dioxide concentration, the factorial analysis examined the effects of temperature, humidity, carbon dioxide loading and scrubber bed (i.e., Bed #1 or Bed #2) on the efficiency of the scrubber (ratio of the difference of the inlet and outlet concentrations to the inlet concentration), bed temperature and the desorption time. Water produced by the scrubber was also collected to obtain some measure of the requirement to handle this water in the exhaust air stream. This analysis was still in progress at the time of the SAMAP 2000 conference and will be reported under separate DCIEM cover.

Conclusions

The experiments showed that even in a pilot plant the amine resin and accompanying technology were reliable enough to operate over 1500 h with minimal downtime. In fact, it was a secondary safety system, a thermistor, which was easily and safely by-passed that failed.

The factorial analysis confirmed the positive correlation of chamber carbon dioxide concentration to carbon dioxide loading and chamber temperature, but, owing to poor humidity control, was unable to show any humidity effects.

The maximum carbon dioxide adsorption capacity was affected by the length of the adsorption cycle. Extending the adsorption cycle beyond the time needed to reactivate the amine bed decreased the average amount of carbon dioxide that could be adsorbed. It was found that reducing the adsorption cycle time to forty minutes increased the allowable carbon dioxide loading to the equivalent to about 4 people (1.6 $L \bullet min^{-1}$). (Further reduction of the adsorption cycle time would have reduced the regeneration of the amine beds, and therefore, would have produced an overall reduction of carbon dioxide load capacity.)

The matching of the empirically determined load capacity to the 4-person capacity used by Astrium to design the scrubber combined with the reliability of the pilot plant suggests that the amine resin technology is mature enough to be considered for full-scale prototype modelling. However, prior to the installation of an amine resin scrubber in a submarine, significant engineering work will be needed to ensure that the submarine has adequate power; space; heating, ventilation and air handling equipment, including water condensers; and an adequate back up system in case of loss of power.

Acknowledgements

I would like to thank Mr. Robert MacLean who wrote the software, assembled the data acquisition equipment and kept it running during this long process. As usual Rob makes all this work possible. I would also like to thank John Hilton and his engineering services support staff for quickly and reliably installing the special services we needed to get the scrubber up and running. Ed Peters's of Ballard help in understanding how the system worked was essential in getting the system up and running and, finally, to keep the experiment running, correct errors and re-program the scrubber controller Lutz Schauer of Astrium was instrumental and I must thank Ed and Lutz for their help.

References

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2. Schauer, Lutz and Andreas Kreis (1993) Air purification systems for submarines. Dornier GmbH, Friedrichshafen, Germany, March 1993.

DEVELOPMENT AND SEA TRIALS OF PROTOTYPE MONOETHANOLAMINE MONITORS FOR USE ON BOARD SUBMARINES

SSA
DERA

GRASEBY
DYNAMICS

SAMAP - October 2000

DPA

SEA
TECHNOLOGY GROUP

Overview

- Introduction
- Continuous monitor
  - Development
  - Sea Trials
- Portable monitor
  - Development
  - Sea Trials
- Conclusions & future work

Introduction

- MEA use
- MEA problems
- MEA monitoring
  - proof-of-concept instrument
  - determination of MEA conc. in CO_2 Scrubber Compartment
  - development & sea trials successful
  - MEA detected in submarine atmosphere

Operational conditions

- Humidity
- Airflow
- Pressure

Requirements

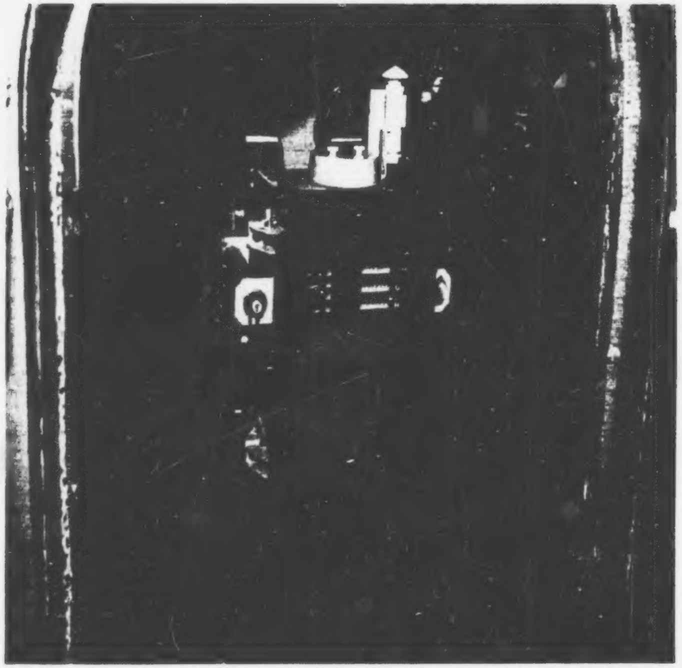
- Monitor MEA
- Obtain continuous real-time profile of MEA vapour concentrations

Monitor preferences

- Real-time monitoring
- Low detection levels
- Sensitivity
- Specific
- Dynamic range relevant to MPCs
- Long term stability of response
- Low power consumption
- Size & weight restricted
- Cost effective
- User-friendly
- Reliable
- Robust

Development of continuous MEA monitor

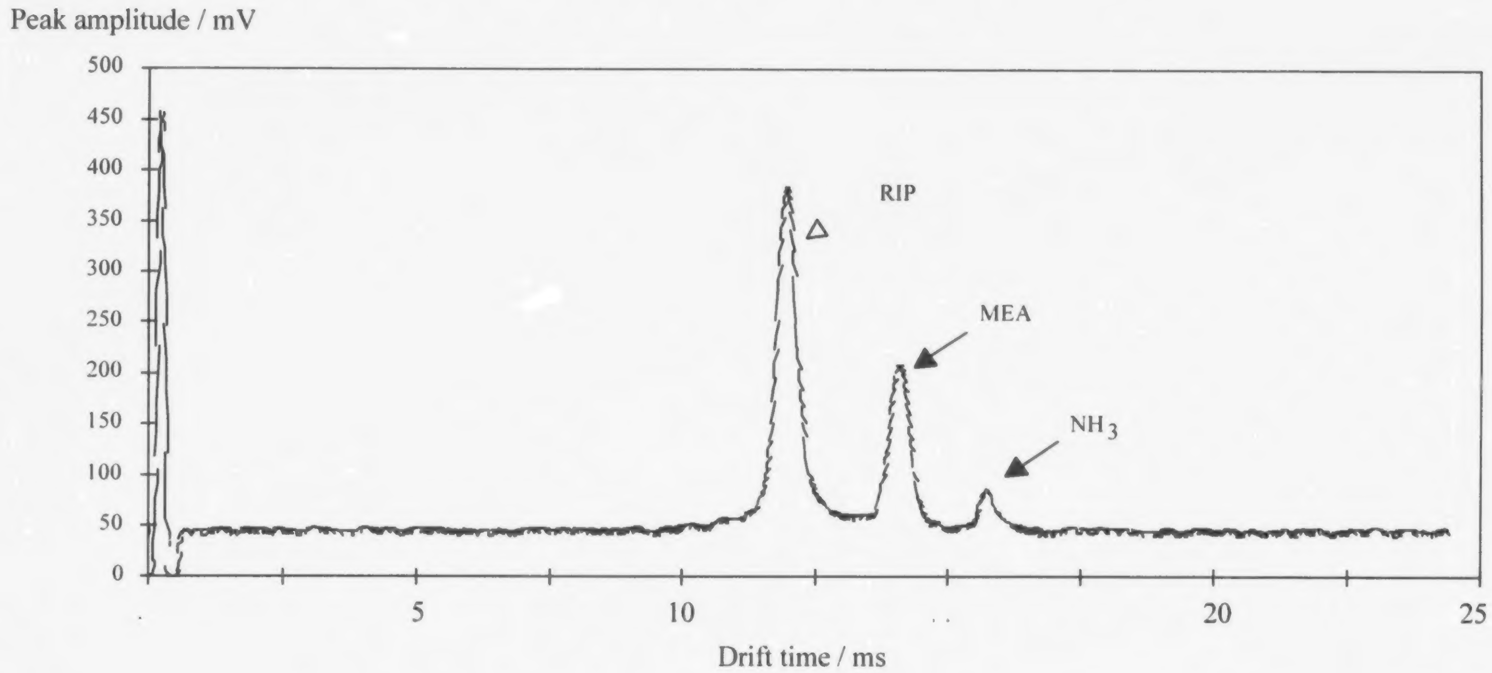
- Laboratory evaluation
  - accuracy
  - precision
  - temperature range
  - effects of humidity
  - specificity
- Sea trials



Continuous monitor results

- Monitor operated continuously for 90 days
- Levels remained below the MPC_{90} except during maintenance

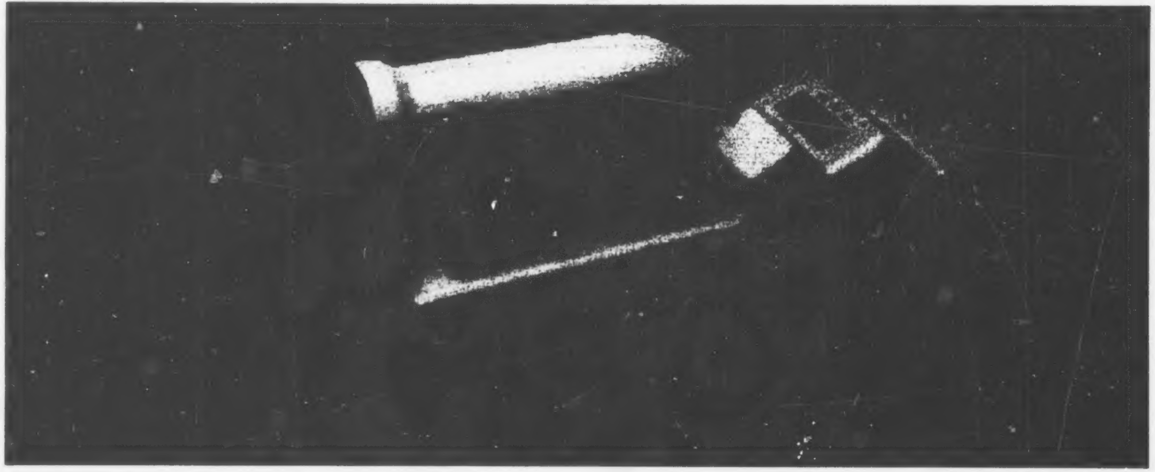
Ion mobility spectrum



Requirements

- Determine MEA concentration in other compartments of the submarine
- Compare conc. on various submarines and scrubber plant
- Portable monitor for MEA

Development of portable monitor



- Modified CAM
  - Direct inlet system
  - 4-Heptanone dopant
  - Software modifications
- Calibration
- Sea trials
  - Recording of readings
  - Collection of spectra
- Post-trials analyses

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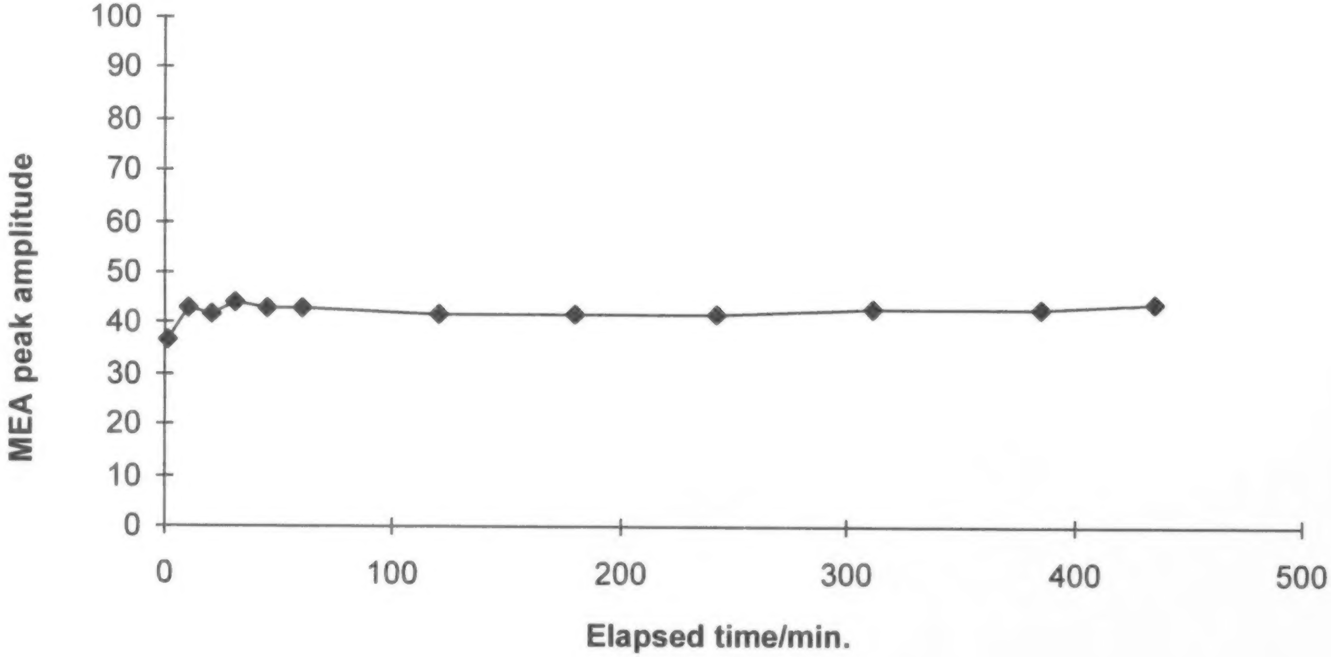
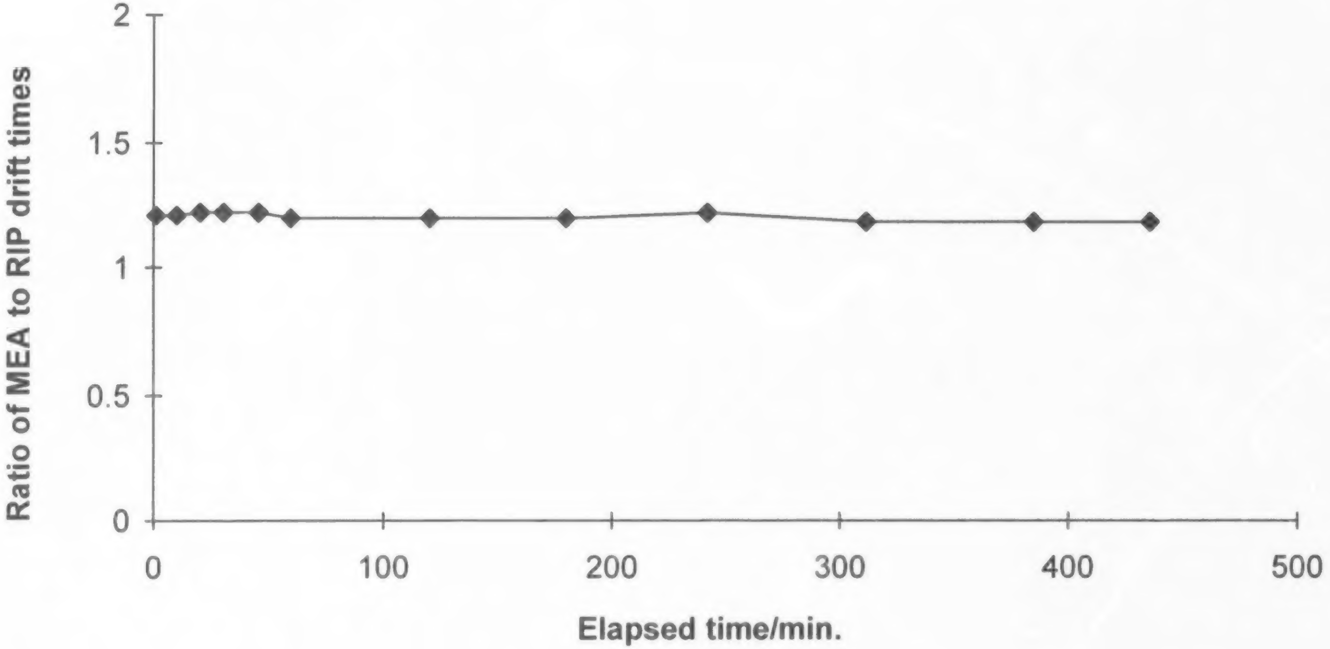
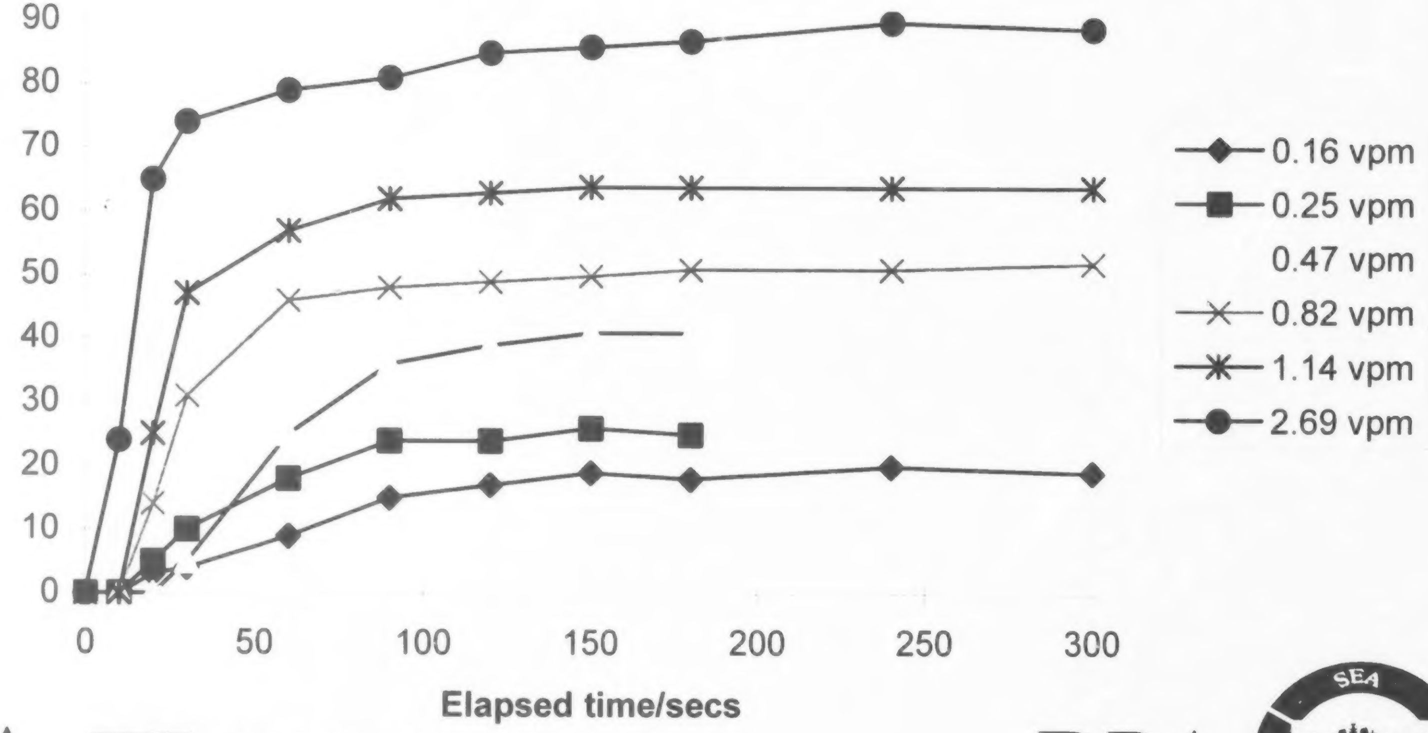
MEA peak amplitude vs time



Ratio of peak positions



Rate of response for different MEA concentrations



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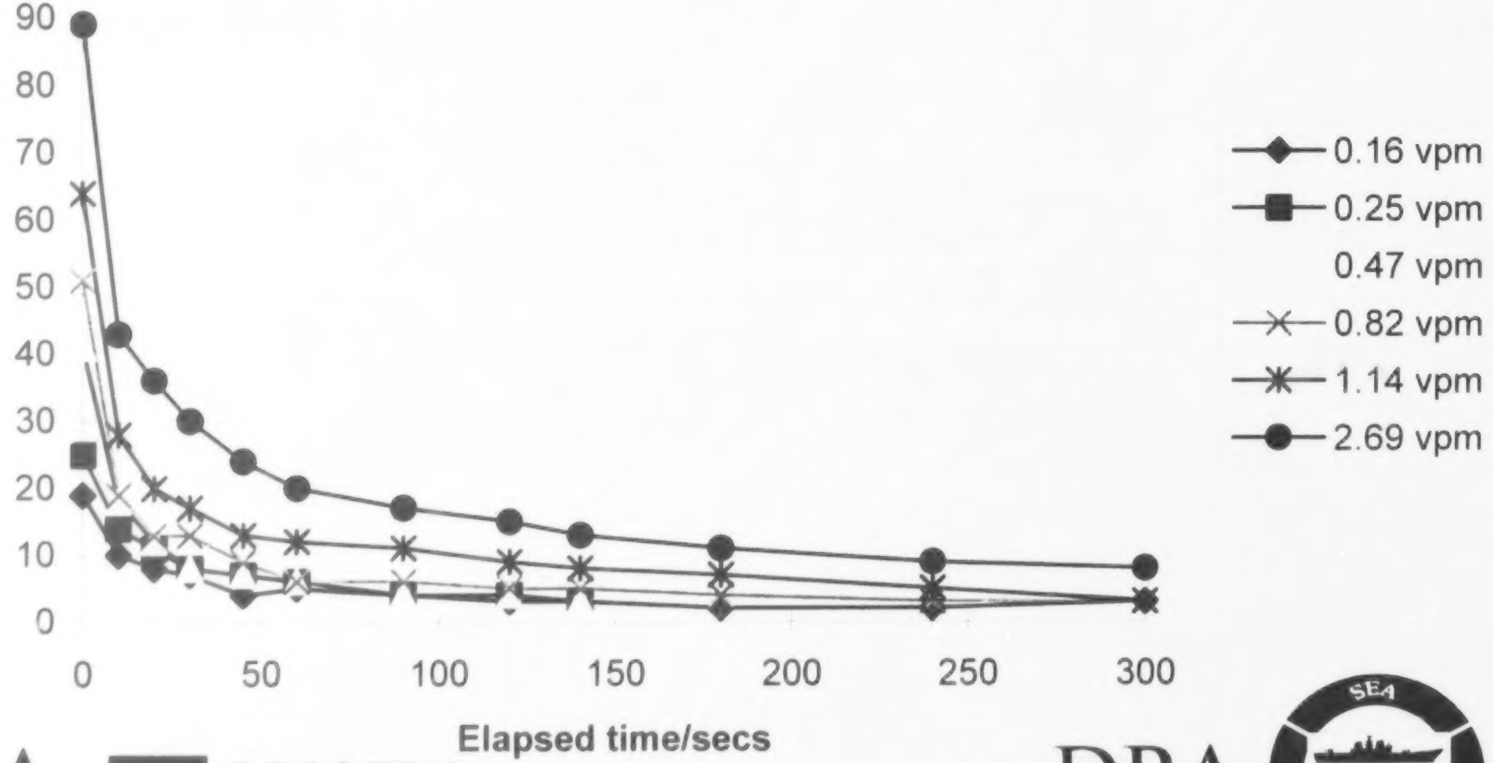
Rate of recovery for different MEA concentrations



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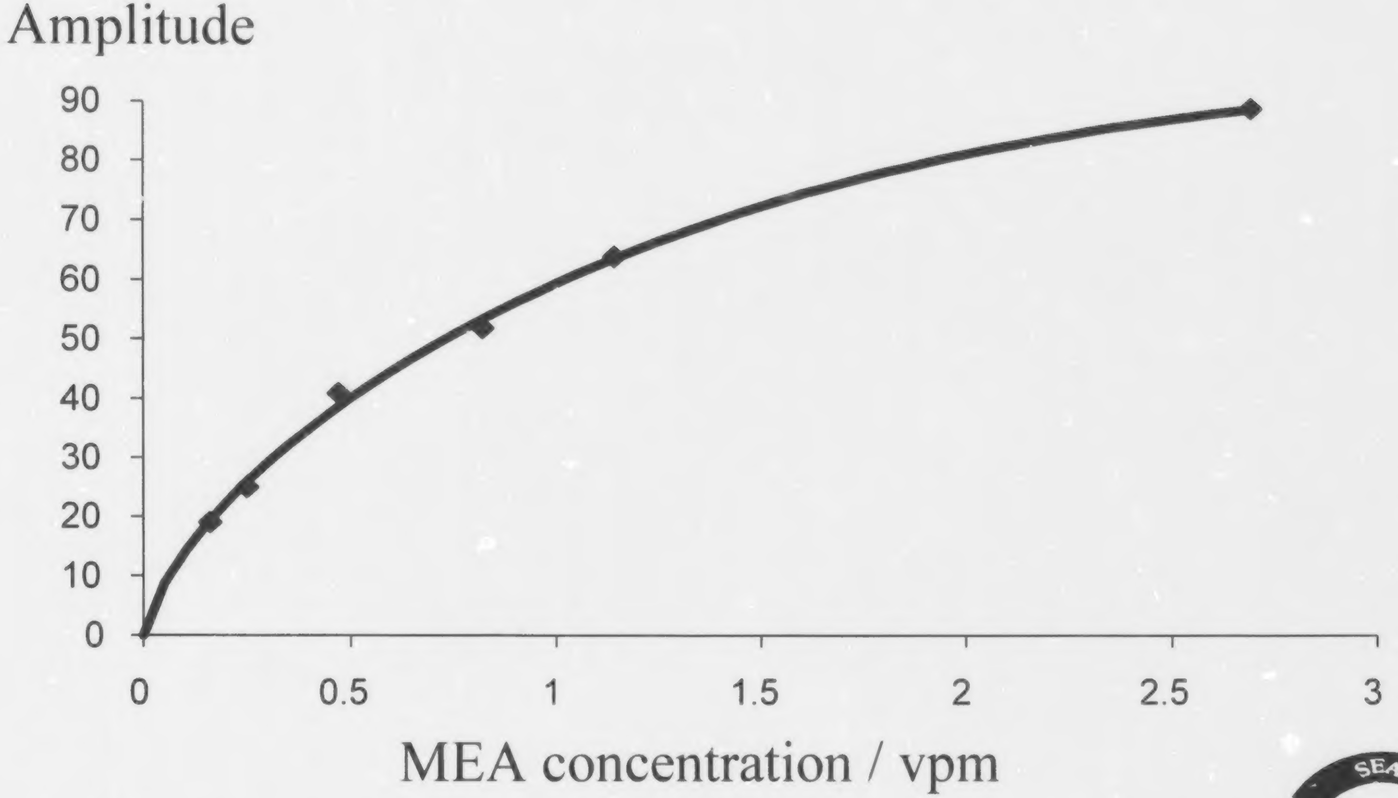
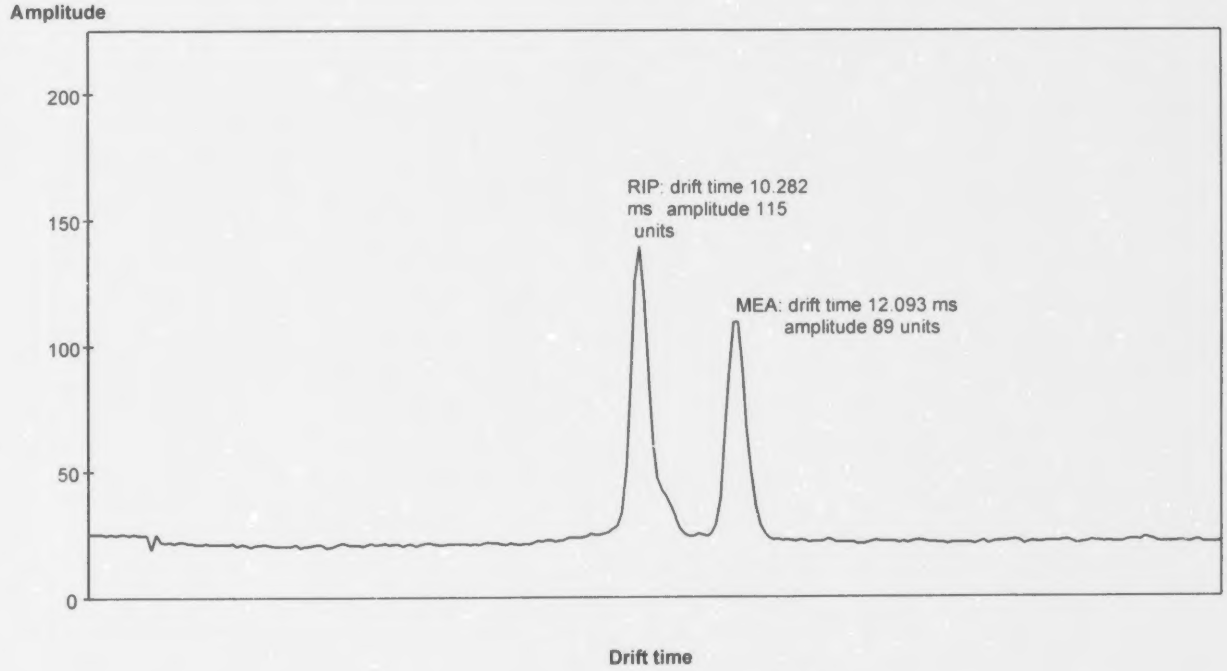
MEA response curve



MEA mobility spectrum



Monitor specifications

- Size: 390 x 145 x 80 mm
- Weight: 2.5 kg incl. Ni/Cd battery
- Extended battery life
- Extended sieve pack life (calculated)
- Limit of detection: 0.05 vpm
- Dynamic range: 0.05 to >2.7 vpm
- 90% response: typically <2 min.
- 90% recovery: typically <4 min.
- Operational temp.: 0° to +40°C
- Storage temp.: -30° to +70°C

Sea trials

- Prior acceptance under laboratory conditions
- Prove functionality of the prototype instrument
- Determine atmospheric concentrations of MEA

Results

- MEA range 0.05 to 2.5 vpm
- Highest conc. in SC
- MEA conc. homogeneous in aft compartment & fwd conc. decreased with distance from SC
- Determined MEA equilibration time

Conclusions

- MEA monitors summary
  - suitable for fixed-point vapour profiling
  - convenient (hand-held)
  - easy to use & robust
  - appropriate for operational requirements
- MEA vapour concentrations in submarines measurable in real-time

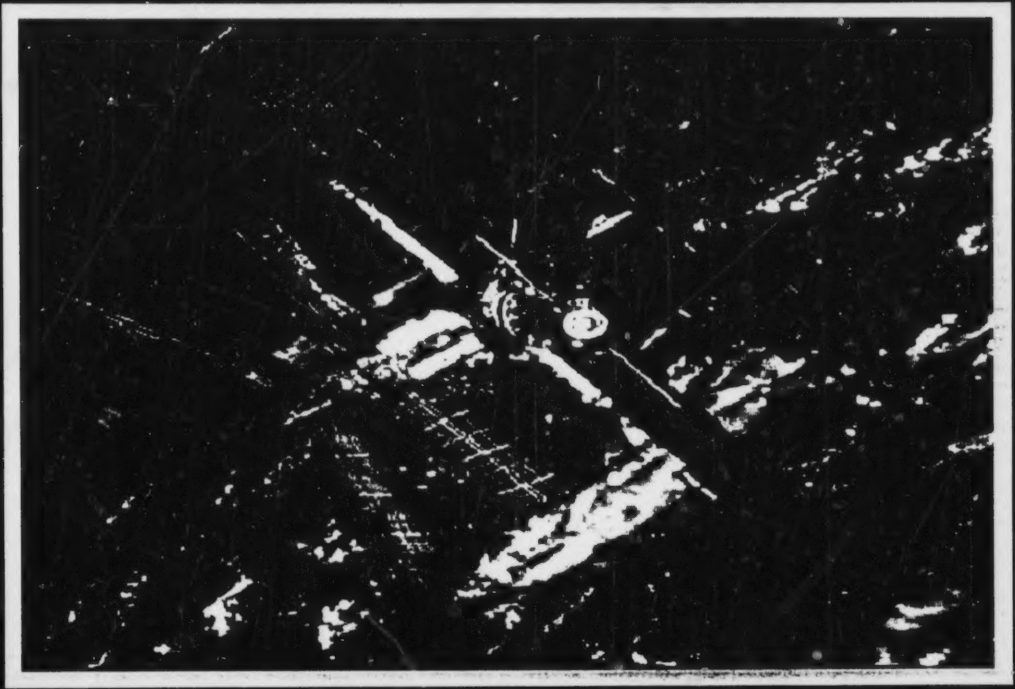
Future work

- Development of stable, long-term dopant source
- Record MEA concentrations in other submarines
- Risk assessment of MEA vapour

Acknowledgements

- Defence Procurement Agency, Sea Technology Group/Submarines
- Marine Auxiliary Environmental & Steam Integrated Project Team (MAES5c)
- Defence Evaluation & Research Agency - Bridgwater Laboratories
- Graseby Dynamics Ltd.
- Defence Science & Technology Organisation Australia

Microbiological Investigations of the Mir Space Station



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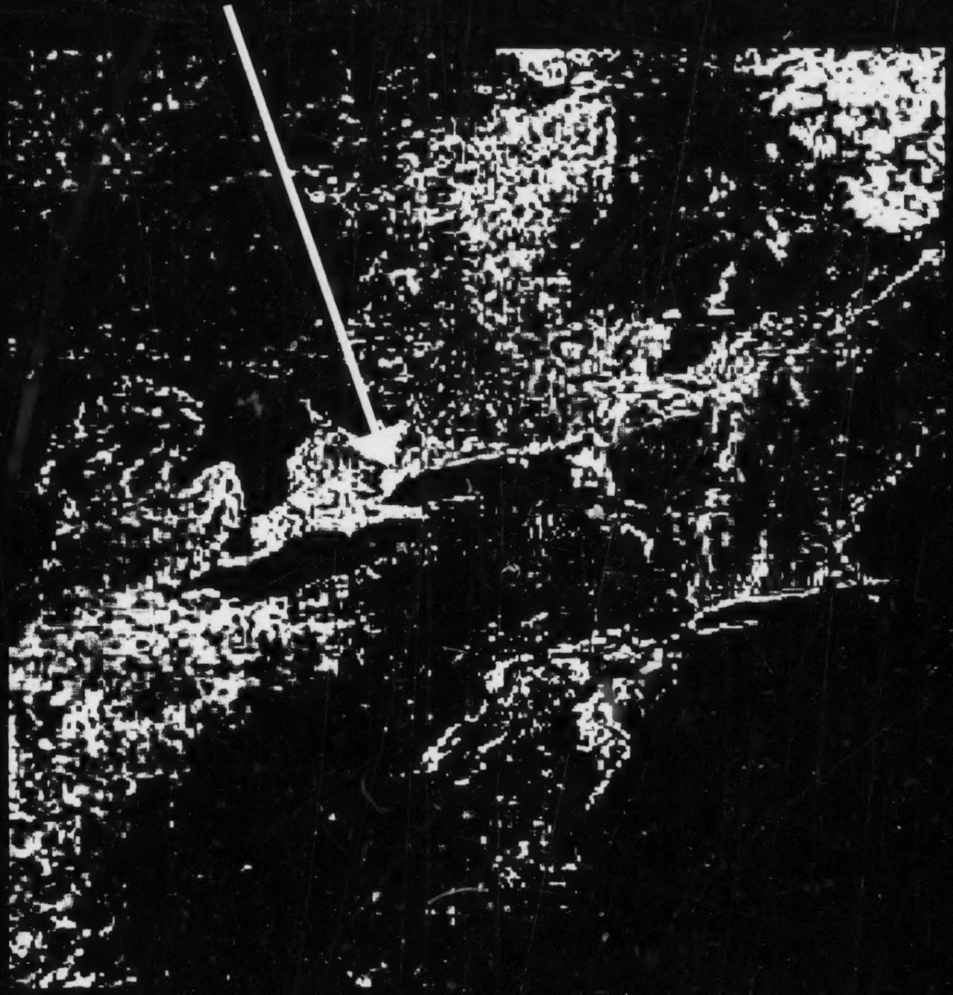
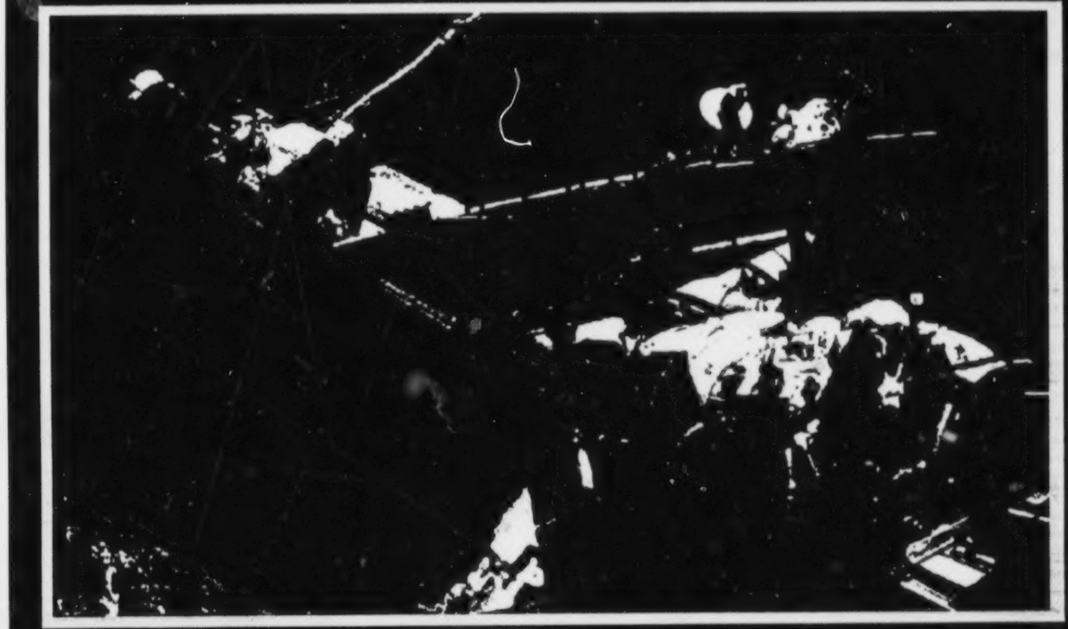


Introduction

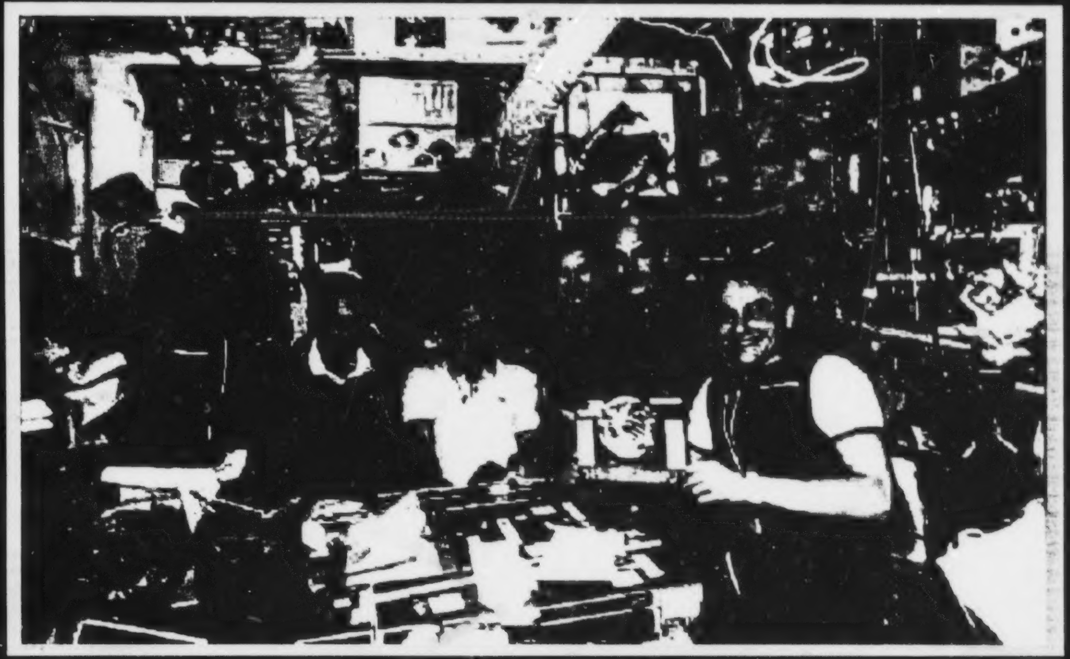
- A study was performed to assess the feasibility of microbial analysis during flight aboard the space station Mir
- Missions lasted from 75 to 209 days
- Samples were acquired from the air, water, surfaces, and crew of both the Mir and orbiter

Objectives



Characterize the microbiota of the crewmembers, air, surface and water before, during, and after a long-duration mission aboard the Mir Space Station

Objectives

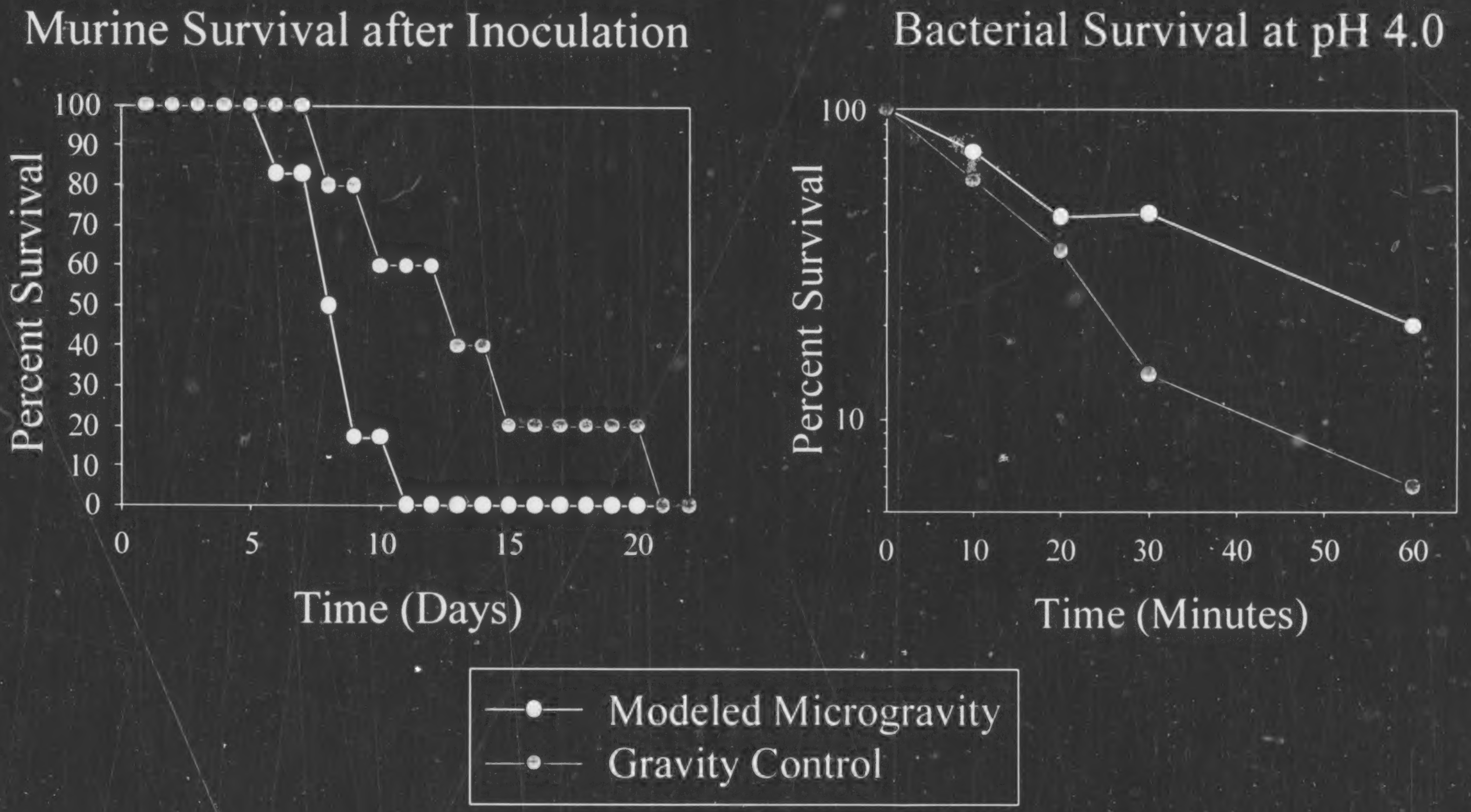


Develop a working relationship with our Russian colleagues in preparation for the International Space Station

Objectives

Have operationally-ready hardware systems ready for the International Space Station

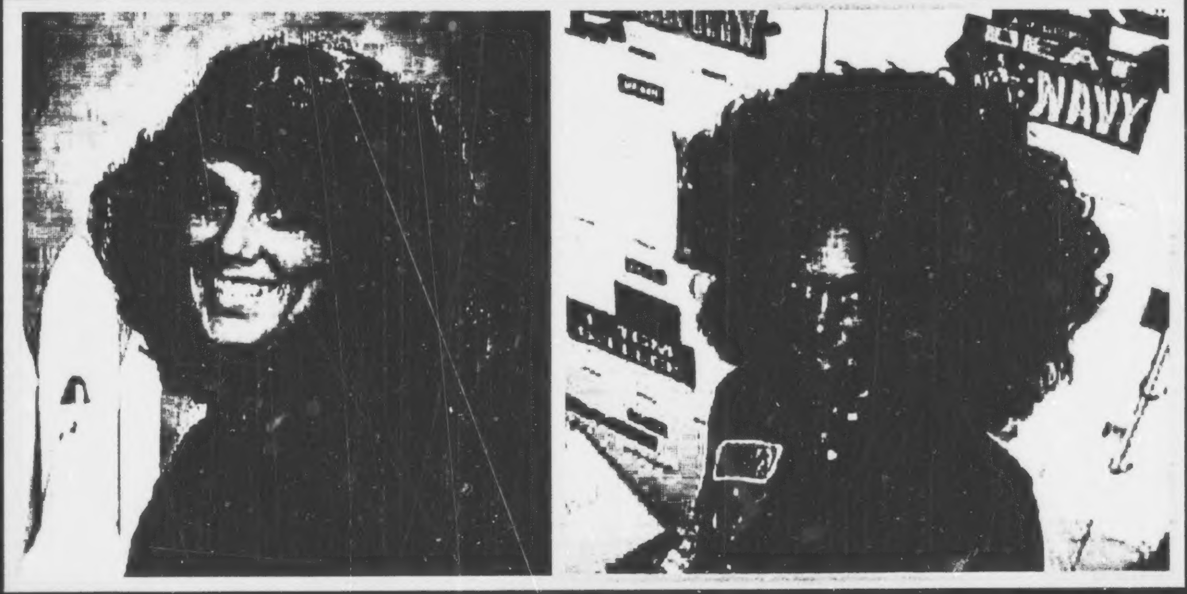
Effects of Microgravity



Murine Survival after Inoculation

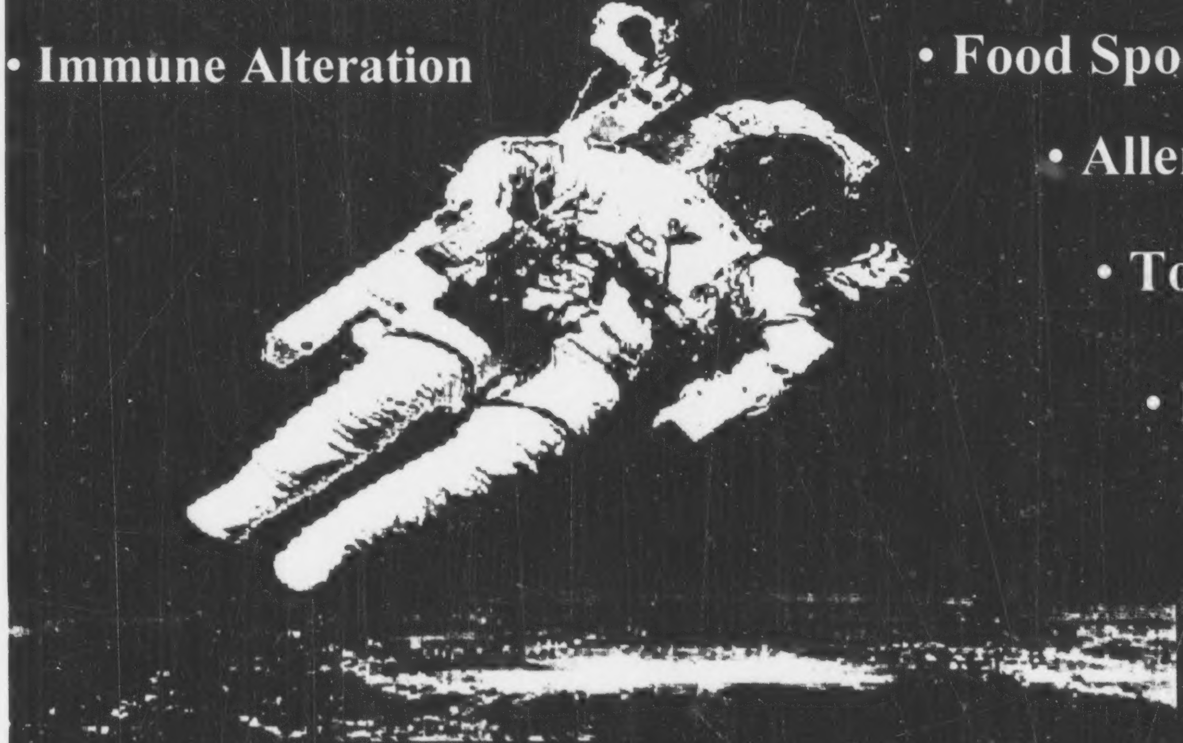
Bacterial Survival at pH 4.0

Effects of Microgravity



Adverse Effects of Microorganisms

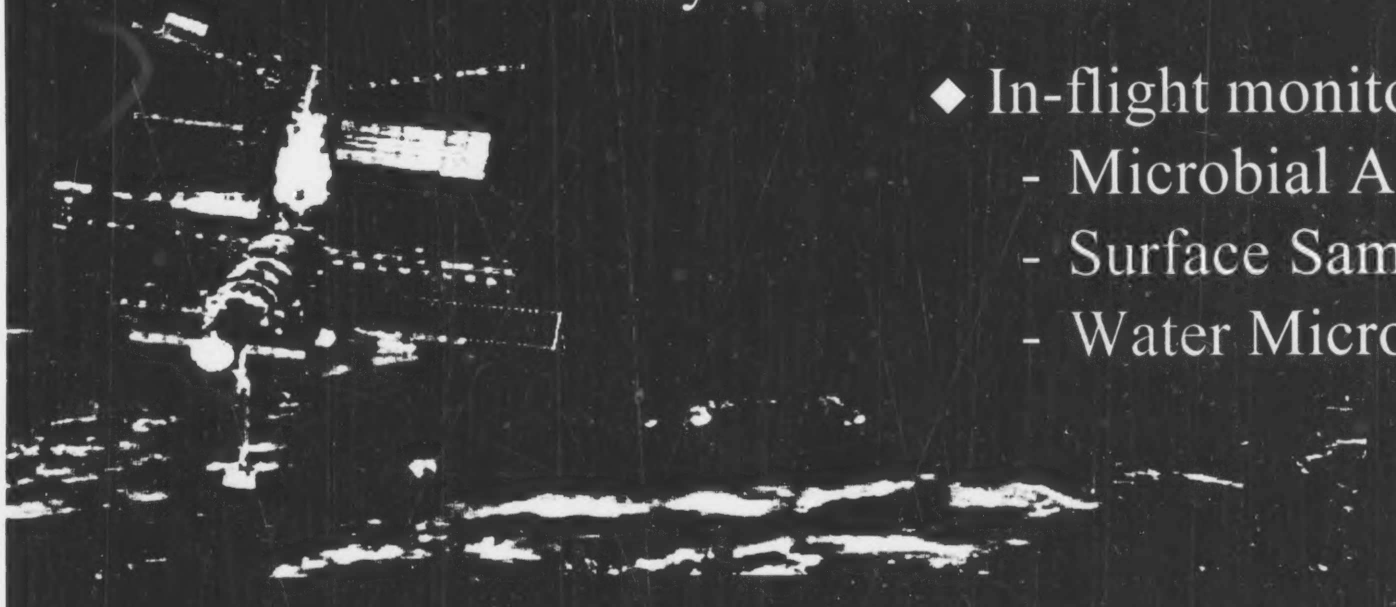
- Infectious Diseases
- Immune Alteration



- Environmental Contamination
- Food Spoilage
- Allergies
- Toxin Production
- Release of Volatiles
- Material Degradation
- Plant Diseases

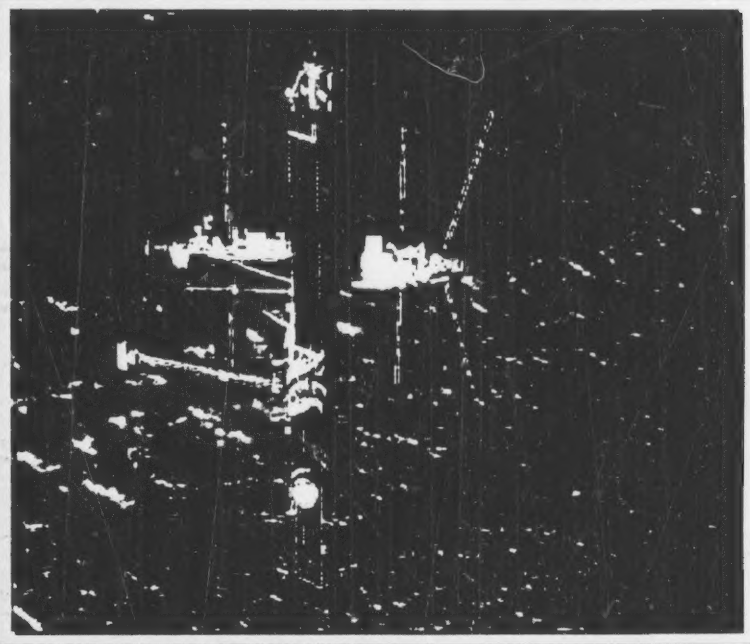
Preventive Measures

- Acceptability standards
- Preflight assessment
  - Crew
  - Environment
  - Payload assessment
- In-flight monitoring
  - Microbial Air Sampler
  - Surface Sampler Kit
  - Water Microbiology Kit



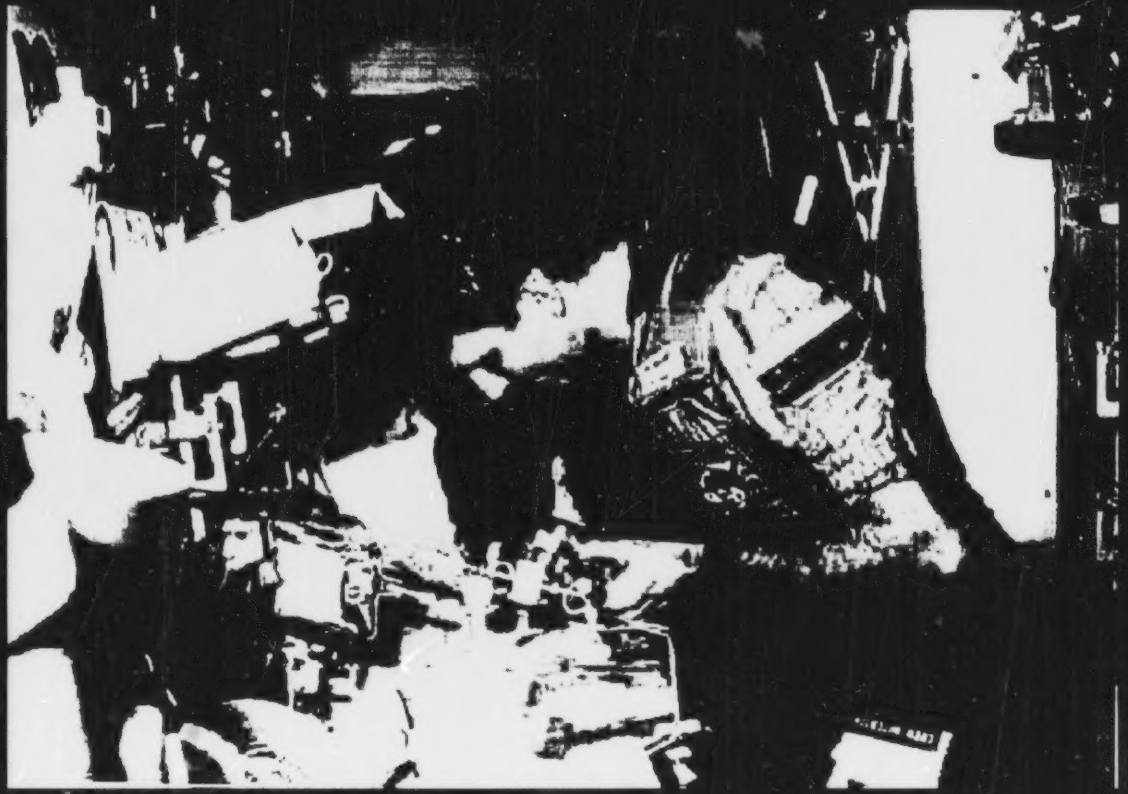
Acceptability Limits

- Air
  - 1000 CFU/ m^3 Bacteria
  - 100 CFU/ m^3 Fungi
- Potable water
  - 100 CFU/100 ml
- Surfaces
  - 10,000 CFU/100 cm^2 Bacteria
  - 100 CFU/100cm^2 Fungi



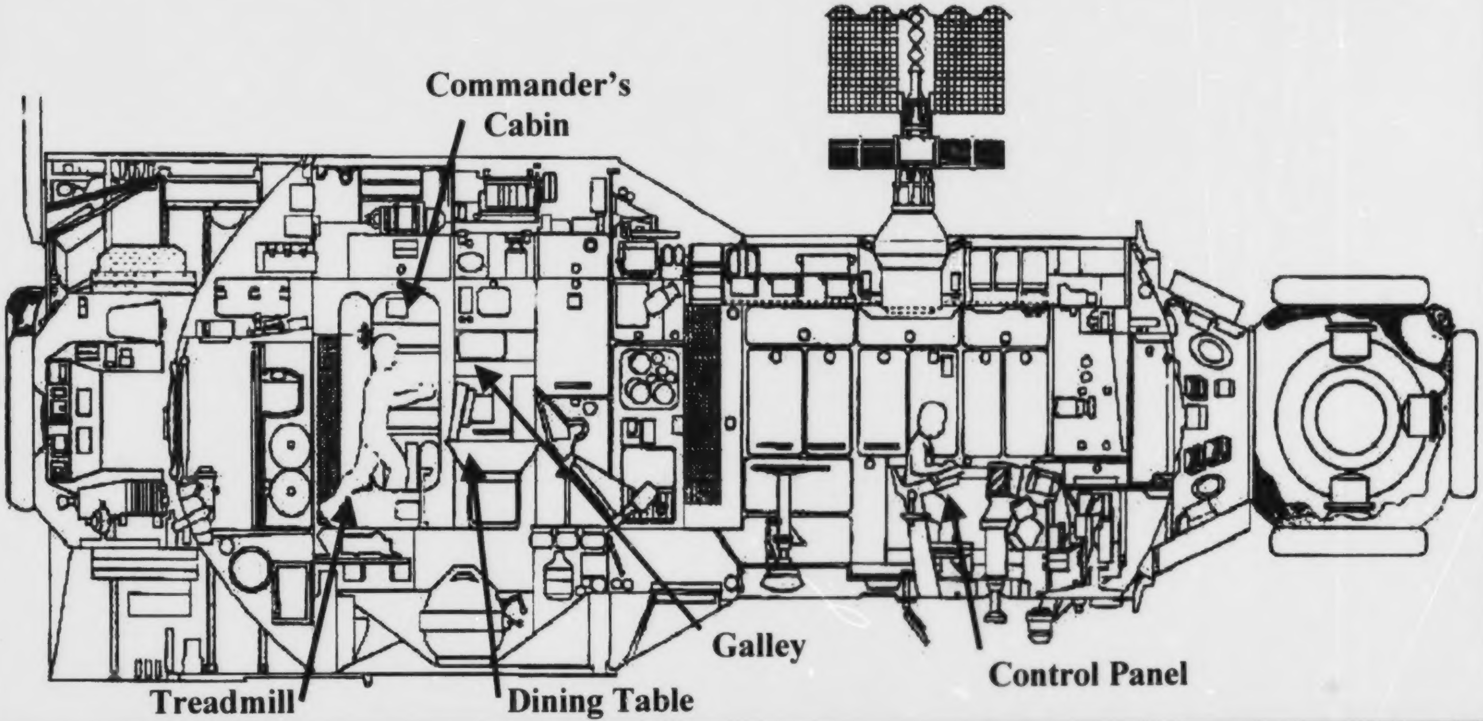
Microbial Analysis of Air during Flight

Microbial Analysis of Water during Flight

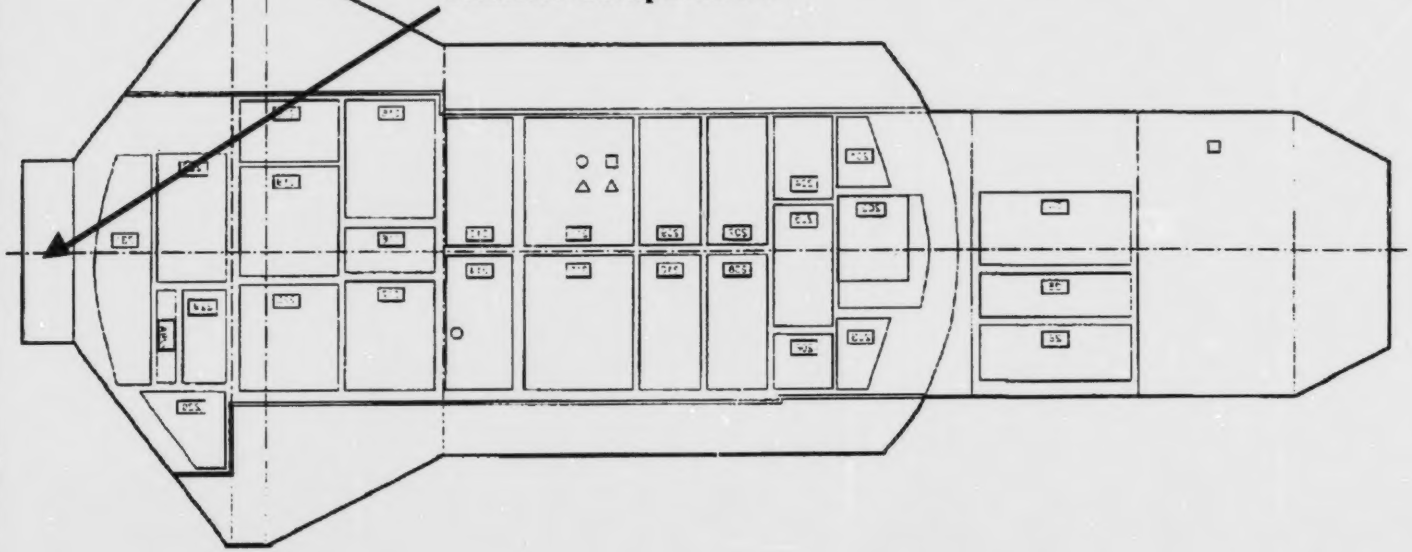


Microbial Analysis of Surfaces during Flight

Core Module

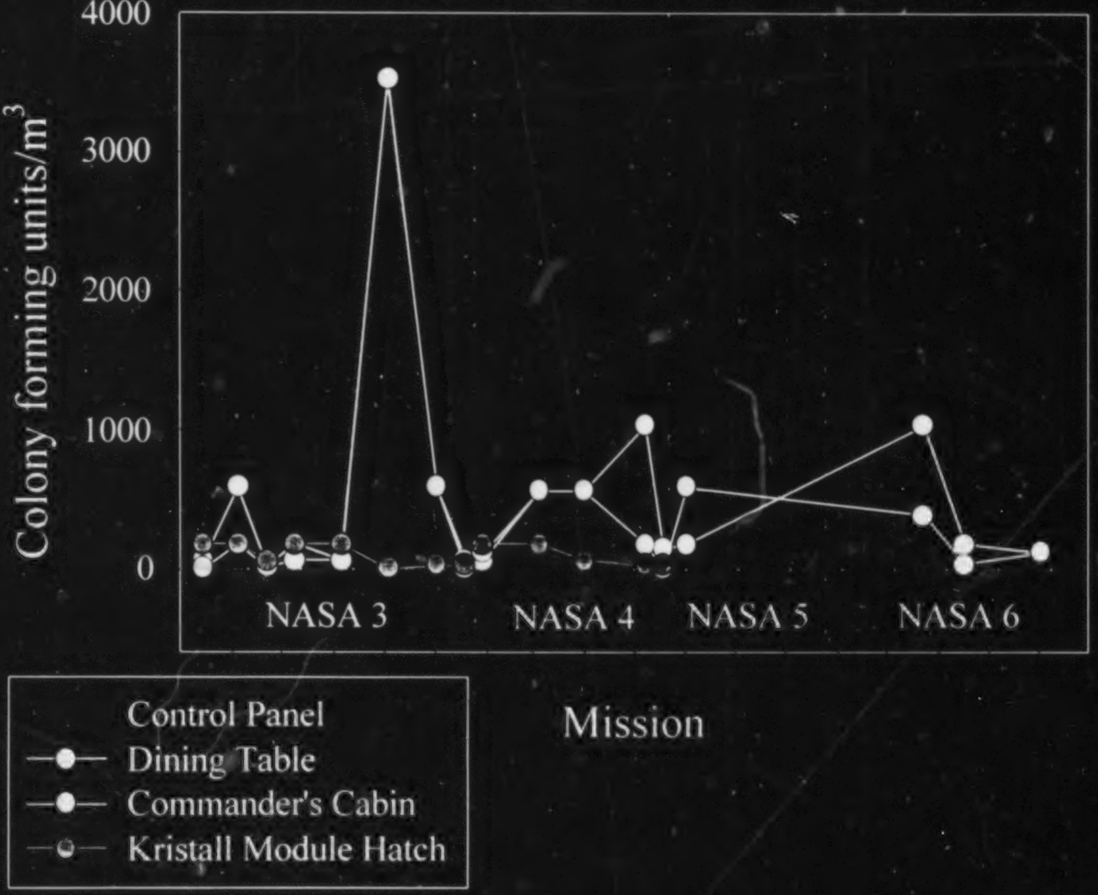

Commander's Cabin
Treadmill
Dining Table
Galley
Control Panel

Kristall Module

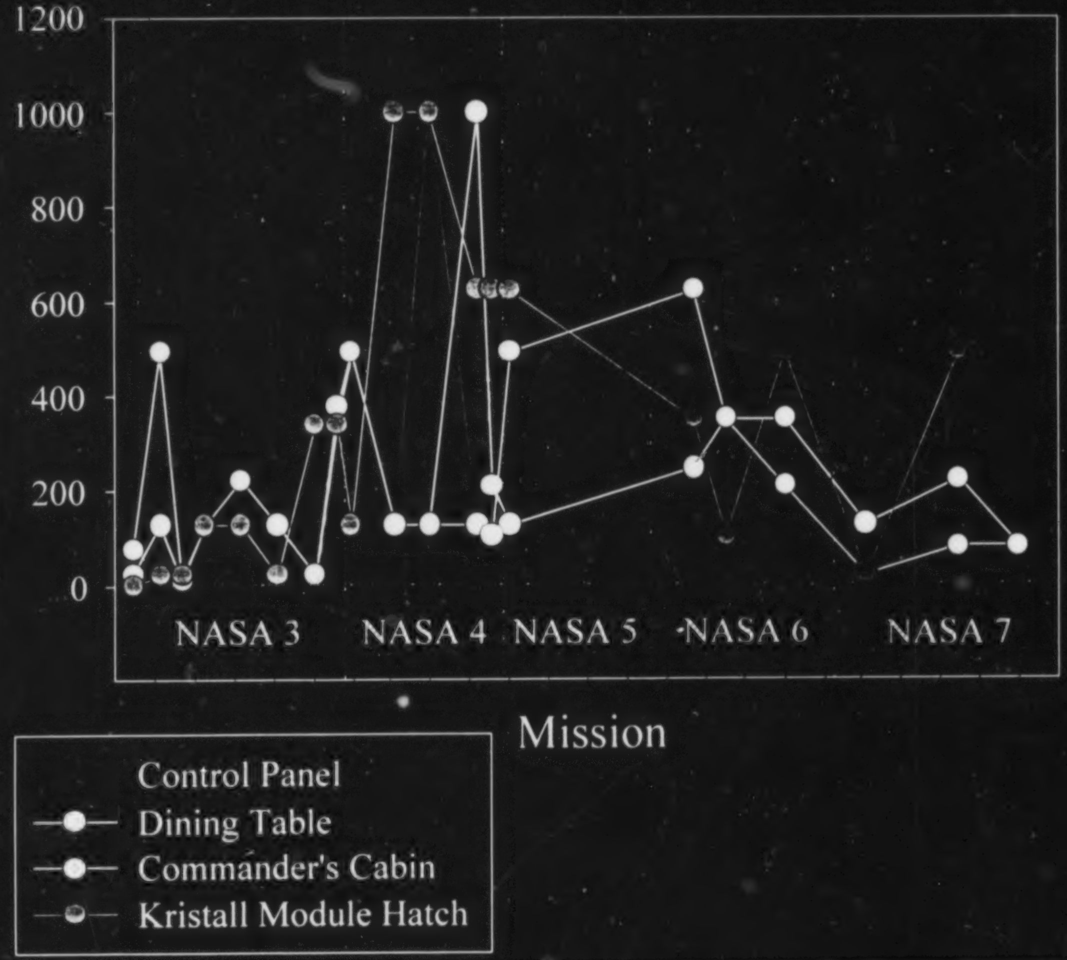


Hatch to
Transfer Compartment

Bacterial Contamination Aboard the Mir Station



Fungal Contamination Aboard the Mir Station



Fungi from MIR
‘Free’ Surface Condensate

NASA 6 “SLIMY” SAMPLE	NASA 7 “SLIMY” SAMPLE	NASA 7 “FRESH” SAMPLE
Acremonium species	*Candida guilliermondii*	*Candida guilliermondii*
Candida guilliermondii	*Candida lipolytica*	*Candida lipolytica*
Candida krusei	*Cladosporium* species	*Fusarium* species
Cladosporium species	*Fusarium* species	*Hansenula anomala*
Fusarium species	*Hansenula anomala*	*Penicillium* species
Penicillium species	*Penicillium* species	*Rhodotorula glutinis*
Rhodotorula rubra	*Rhodotorula glutinis*	*Rhodotorula rubra*
	Rhodotorula rubra	

Aerobic Bacteria from MIR 'Free' Surface Condensate

NASA 6

"SLIMY" SAMPLE

Alcaligenes eutrophus
Alcaligenes latus
Citrobacter freundii
Corynebacterium aquaticum
Corynebacterium jeikeium

Escherichia coli

Methylobacterium species
Pseudomonas vesicularis
Serratia liquefaciens
Unidentified gram negative rod
Xanthomonas maltophilia

NASA 7

"SLIMY" SAMPLE

Alcaligenes faecalis
Bacillus circulans
Bacillus coagulans
Bacillus licheniformis
Bacillus pumilus
Bacillus species
CDC Group IVC 2
Citrobacter brackii
Citrobacter freundii
Comamonas acidovorans
Corynebacterium species
Flavobacterium meningosepticum
Presumptive *Legionella* species

Serratia marcescens

Yersinia intermedia

NASA 7

"FRESH" SAMPLE

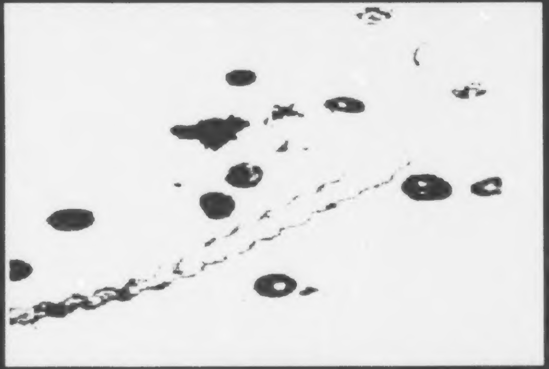
Bacillus coagulans
Bacillus licheniformis
Bacillus pumilus
Bacillus species
Comamonas acidovorans
Corynebacterium species

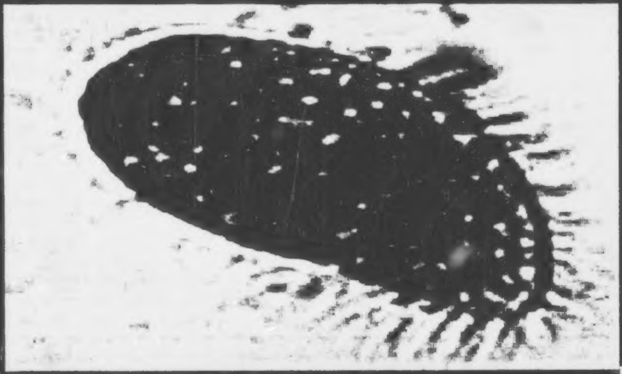
Presumptive *Legionella*

Serratia liquefaciens
Serratia marcerans
Sphingobacterium thalpophilum
Unidentified gram negative rods (4)
Yersinia frederiksenii
Yersinia intermedia

Found in MIR
'Free' Surface Condensate

Spirochetes





Ciliated Protozoa

Dust Mites

Lessons Learned

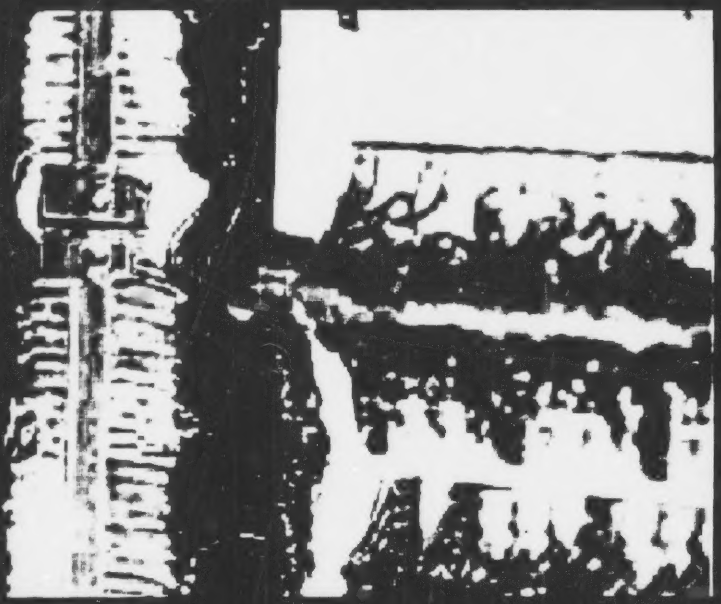
- Stringent preflight monitoring of crew is necessary to assure maintenance of health, safety, and optimum performance
- Rigorous preflight monitoring of water, food, biologicals, and selected hardware to minimize contamination of ISS is necessary
- Improper functioning of life support systems (e.g. temperature and humidity control) can influence microbial levels

Lessons Learned

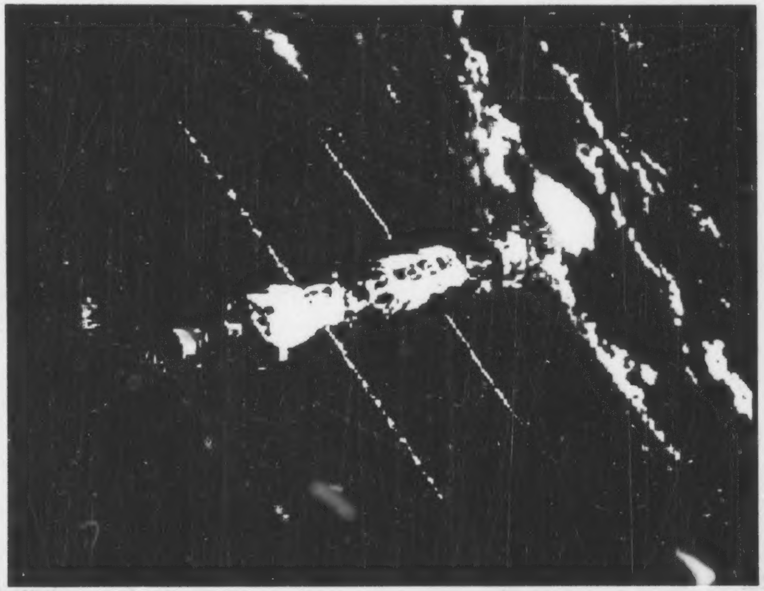
- Provision of monitoring capabilities to verify a safe environment is essential
- Housekeeping is of paramount importance for the maintenance of a healthy living environment

Lessons Learned

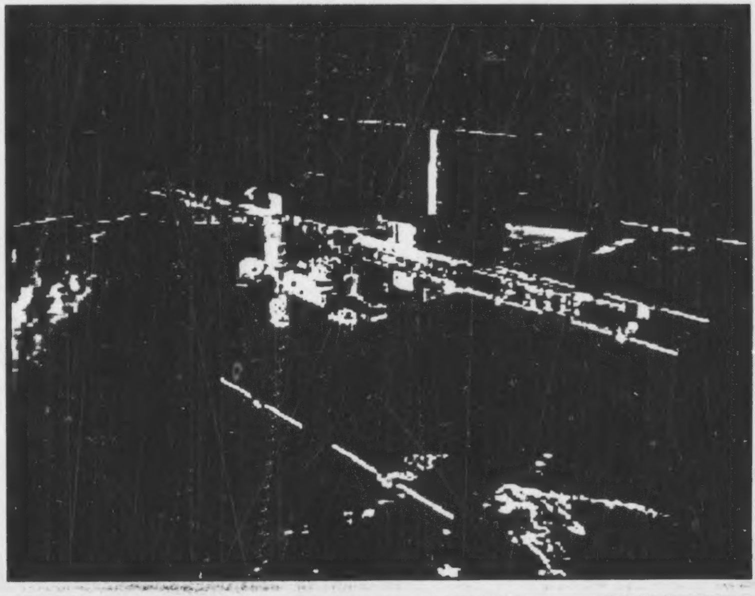
- ◆ Microorganisms play a key role in the biodestruction of materials and can contribute to equipment and hardware malfunctions



The International Space Station



Current



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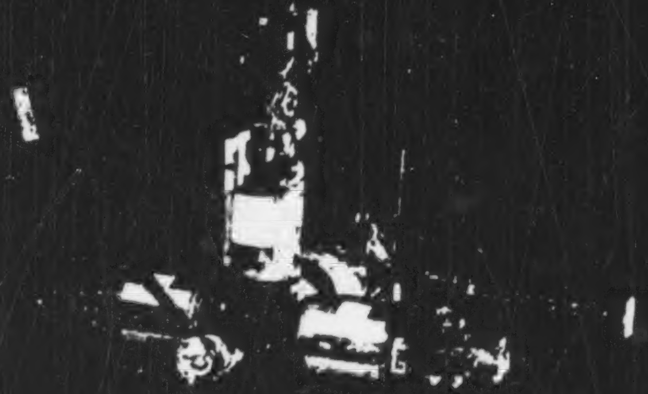

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NASA 2
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NASA 4
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Toxicity of 2,6-Di-*tert*-butyl-4-Nitrophenol (DBNP)

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[5]Mobil Business Resources Corp., Paulsboro, NJ

WHAT IS DBNP?

- Yellow Substance
- Submarine Contaminant
- Nitrated DBP from Oil Mist

WHY IS DBNP A NAVY ISSUE?

- Spread Throughout Submarines by Venting
- Visible on Bulkheads, Bedding, Skin
- DBP, an Antioxidant additive was removed
- Recent laboratory animal results show increased levels of toxicity than reported.

EXPOSURE DATA

- Submarine atmosphere analysis of 24-hour exposure concentrations < 3.0 to 122 ppb.

- Laboratory rat oral effects levels for acute toxicity are 0.175 to 17.53 ppb.

- DBNP is poorly absorbed through the skin.

RESULTS OF LABORATORY ANMIAL STUDIES

- DBNP is slowly absorbed and not metabolized

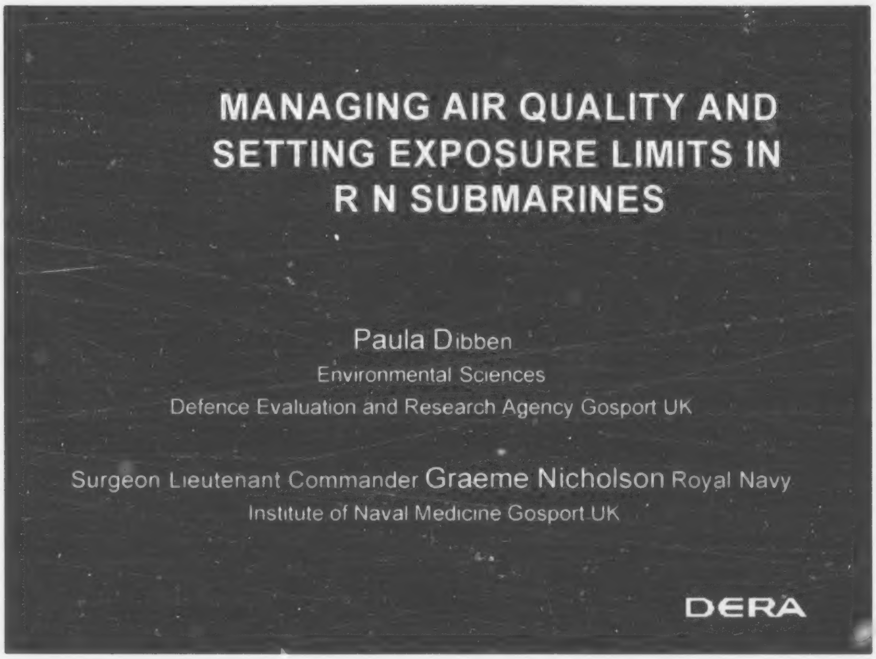
- Oral toxicity is much higher than reported. (50 - 80 mg/kg body weight compared to 500 mg/kg body weight).

- Mechanism of action is considered to be disruption of the normal cell energy, by uncoupling ATP.

- Studies to confirm this are planned

CONCLUSION

- DBNP is more toxic in rats than is reported.
- The health risk from DBNP in submarines is currently unresolved.
- Future research will define absorption, distribution, metabolism and excretion to help define target organ toxicity.
- Further research is necessary to clarify the human health risk of DBNP.



MANAGING AIR QUALITY AND SETTING EXPOSURE LIMITS IN R N SUBMARINES

Paula Dibben
Environmental Sciences
Defence Evaluation and Research Agency Gosport UK

Surgeon Lieutenant Commander Graeme Nicholson Royal Navy
Institute of Naval Medicine Gosport UK

DERA

I am Sgn Lt Cdr Graeme Nicholson of the Institute of Naval Medicinecurrently holding the post of Medical Officer Submarine Medicine. I am responsible for the medical aspects of this work

I am joint author of this paper with Paula Dibben, until recently a Principal Scientist in Environmental Sciences department of DERA. She is a chemist who has worked in atmosphere control in enclosed environments for more years than she care to recall! She is unable to be here this week as she has recently changed jobs to work with the MOD on scientific information exchange programmes.

The aim of this short presentation is to outline the RN philosophy on setting exposure limits to control contaminants and to highlight techniques which have been developed to sample those substances about which we have health concerns.

INM and DERA have a close working relationship both informally and formally through the Ministry of Defence Submarine Air Purification Committee and its Subcommittees. Several of the speakers here from the UK sit on these committees and are intimately involved in the work being described. These committees draw together all MOD experts with an interest in submarine atmosphere control both setting the policy and being responsible for ensuring that suitable hardware is available to maintain good quality air in the enclosed atmosphere of RN submarines.

Sources of submarine contamination

Submarine allows ~23m^3 air per man

Each man consumes 28 l/Hour of oxygen

Each man produces 20 l/Hour of carbon dioxide

Carbon monoxide is produced by cooking, smoking and hot oils

Hydrogen is produced by battery charging

Organic vapours are produced by paints, cooking, adhesives, lighter fluid, refrigerant leaks, etc.

Aerosols arise from machinery and smoking

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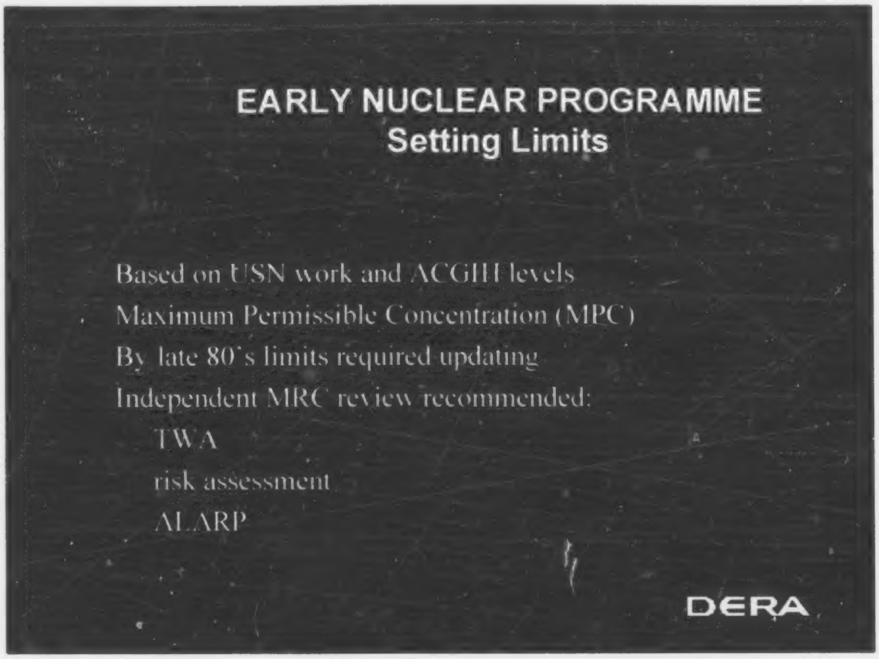
Enclosing up to 180 people in a sealed tube for periods potentially in excess of 90 days brings obvious problems in maintaining an atmosphere to support life, and less obvious problems in dealing with the large number of low level contaminants encountered. Whilst the toxicology of many substances is well known, at short term high level exposure levels, the consequences to human health of exposure to low concentrations of complex mixtures of contaminants is less well understood. The MOD maintains its duty of care in ensuring that trace contaminants are monitored and the concentrations recorded.

READ

CO arises from cooking, and from hot machinery oils.RN submarines are still allowed to smoke tobacco during patrol so in addition to the products of the combustion of tobacco carbon monoxide is generated (100ml/cigarette).

Organic vapours and aerosols arise from many sources. The men import chemicals for washing and cleaning themselves and their clothes which may elute solvents . The materials used in the building, maintenance and running of the submarine will contribute to the background organic vapours and aerosols which will build up and will degrade the air quality during patrol.Any of these contaminants may undergo chemical changes by interacting with other atmospheric components or with the equipment on board.

This situation is comparable to that in any enclosed environment and a regime of air purification and monitoring is required to maintain air quality throughout patrol.



EARLY NUCLEAR PROGRAMME
Setting Limits

- Based on USN work and ACGIH levels
- Maximum Permissible Concentration (MPC)
- By late 80's limits required updating
- Independent MRC review recommended:
  - TWA
  - risk assessment
  - ALARP

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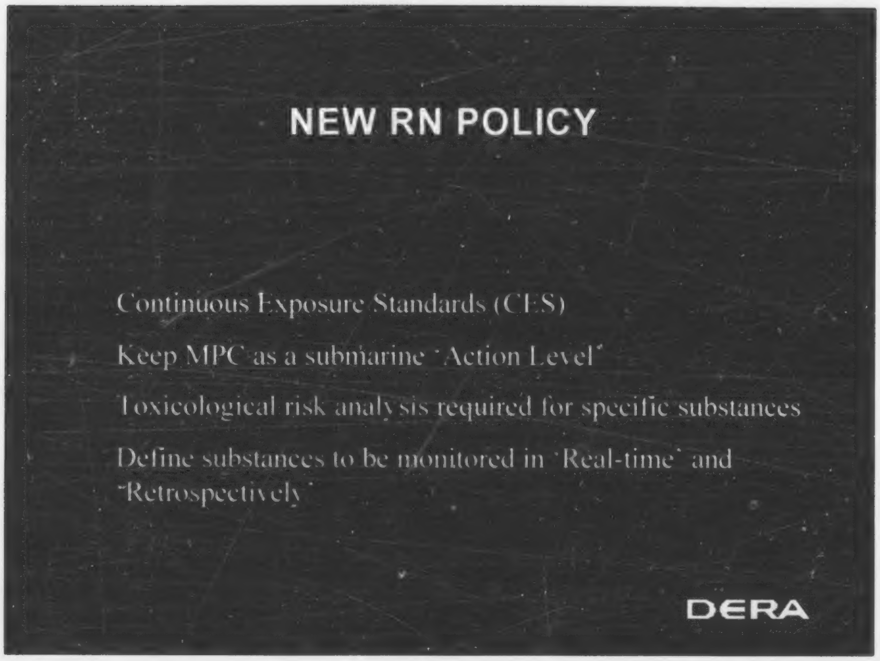
Early non nuclear submarines required either to surface or draw in air through a snort mast on a daily basis. This process refreshed the submarine air by replacing oxygen and clearing contaminants. Few contaminant exposure limits were available .

The introduction of Nuclear Propulsion and the possibility of unlimited submerged endurance, however, heralded the requirement for limits to be set both for the major physiological gases to support a functioning crew, and for the low level contaminants to avoid the possibility of inducing ill health over a longer period in submariners.

UK followed US both in nuclear propulsion systems on submarines and by accepting the concept of Maximum Permissible Concentrations (MPCs). These are limits set at levels believed to be physiologically 'safe', and achievable with the air purification equipment available. These limits were initially based on the ACGIH industrial exposure limits with some subtle transatlantic alterations.

Whilst the system was found to be a workable and safe and stood the test of time, by 1985 it was obvious that a major review of our policy was required in order to keep pace of developing EEC and UK legislation on Health and Safety and Control of Substances Hazardous to Health.

An independent body the Medical Research Council was requested to review RN system and they recommended that we used TWA, a method of risk assessment to keep levels to the ALARP principle. It is worth noting too that the MRC stated that the RN had done a good job in the past and that their medical experts were best placed to set new exposure levels !



NEW RN POLICY

- Continuous Exposure Standards (CES)
- Keep MPC as a submarine 'Action Level'
- Toxicological risk analysis required for specific substances
- Define substances to be monitored in 'Real-time' and 'Retrospectively'

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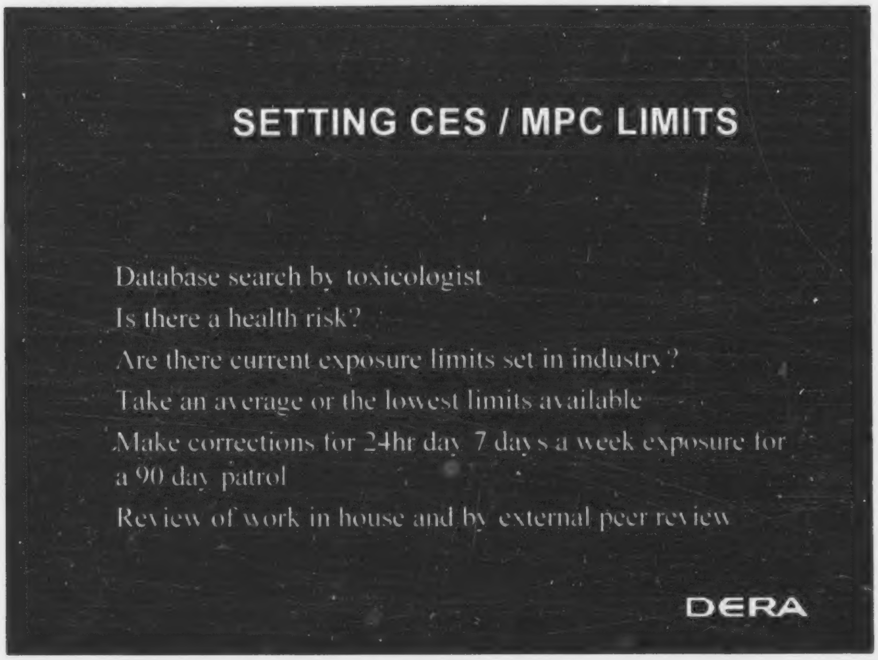
So taking account of the MRC comments , INM decided to set a Submarine Occupation Exposure Standard called a Continuous Exposure Standard (CES). It is defined as **A 24-hour time weighted average concentration that may be safely inhaled day after day for the duration of a submarine patrol lasting around 90 days .**

However, as TWA calculations could be complex to conduct , record and justify in an operational scenario it was decided to continue to issue the standard as MPCs or 'ACTION LEVELS' for patrol duration. These MPCs are a series of ceiling limits requiring specific action either to avoid exceeding them or to recover the situation if exceeded.There are 3 levels ….one set for 60mins, 24hrs and 90days.

To decide if an MPC is needed and to set one a 'risk assessment' taking into account the toxicity of the material, the fact that it is known to be onboard, the possibility of it being produced in a fire etc. is undertaken. This has produced a series of lists of substances which require to be monitored either in real time or retrospectively.



SETTING CES / MPC LIMITS

- Database search by toxicologist
- Is there a health risk?
- Are there current exposure limits set in industry?
- Take an average or the lowest limits available
- Make corrections for 24hr day 7 days a week exposure for a 90 day patrol
- Review of work in house and by external peer review

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The INM are responsible for setting these exposure levels and the process is performed in stages.

Database search by toxicologist

Is there a health risk?

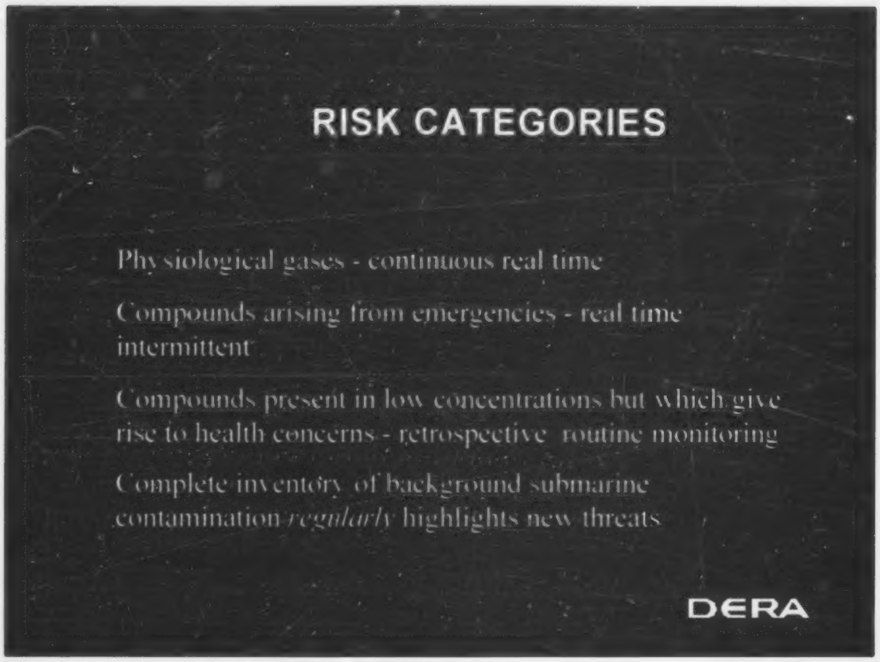
Are there current exposure limits set in industry?

Take an average or the lowest limits available

Make corrections for 24hr day 7 days a week exposure for a 90 day patrol

Review of work in house and by external peer review

Completed reports are circulated in house to a committee of scientists, medics, operators and the personnel responsible for atmosphere monitoring and atmosphere purification equipment for comments, changes and approval. Should the item be either controversial, or there be limited data to complete the work on then the reports will be sent out to peer review by a H&SE expert in the field who has long experience in setting European exposure standards.



RISK CATEGORIES

Physiological gases - continuous real time

Compounds arising from emergencies - real time intermittent

Compounds present in low concentrations but which give rise to health concerns - retrospective routine monitoring

Complete inventory of background submarine contamination *regularly* highlights new threats

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These substances which have been designated CES / MPC values then need to grouped according to how acute is the health risk . Once this has been done we can decide whether monitoring is required in real time and whether it needs to be conducted continuously or occasionally.

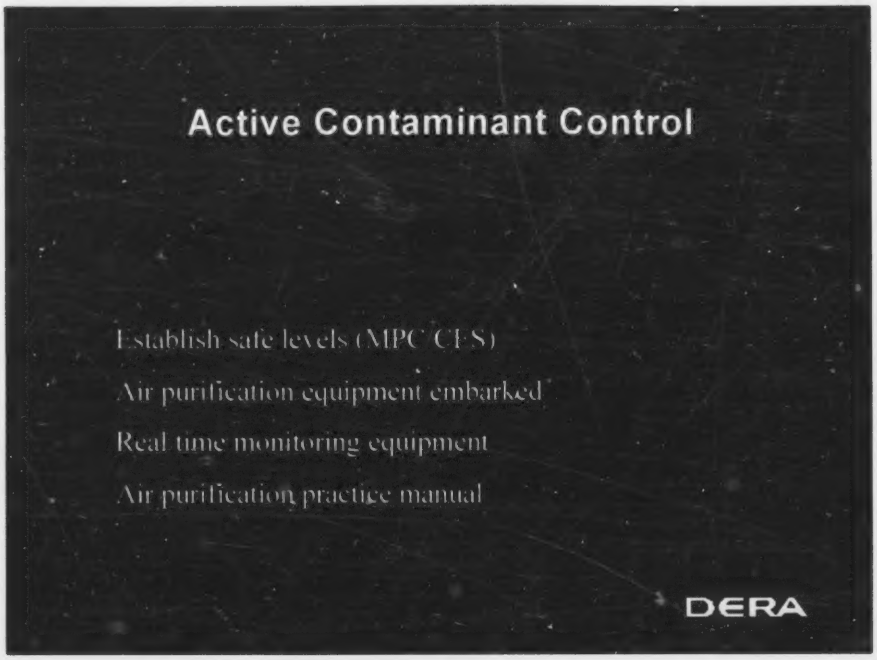
For example the physiological gases along with hydrogen (an exposure risk), and the halogenated hydrocarbons need to be monitored in real time continuously.

Compounds of toxicological importance arising as a result of an emergency e.g. fire need to be monitored intermittently as required but in real time.

Substances with low background levels for which there is reasonable evidence of toxicity will not have acute health effects and may be monitored post patrol but routinely.

Additionally we need to get a handle on any new threats to the atmosphere.

We needed some techniques which could meet these needs.



Active Contaminant Control

Establish safe levels (MPC/CES)

Air purification equipment embarked

Real time monitoring equipment

Air purification practice manual

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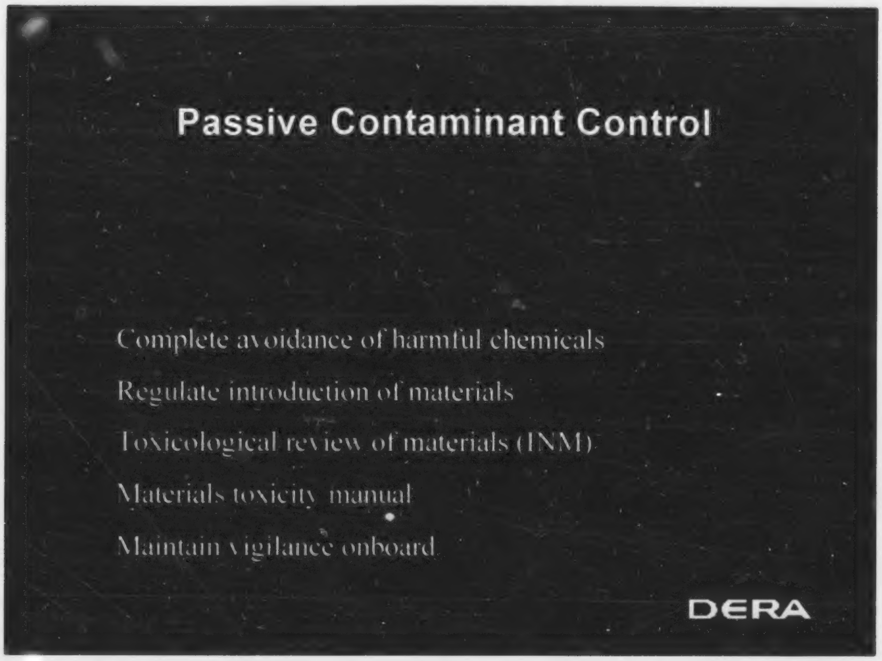
Two methods of control of the submarine atmosphere contaminants are in place. Obviously we need an active method for the removal of the physiological gases during patrol.

Once the exposure limit has been set and a suitable air purification system is embarked to remove that contaminant , we need a method of real time monitoring to ensure that limit is not exceeded

The air purification manual sets out the instructions on the operation of the Air Purification equipment and the procedures to be employed if any breaches of the exposure limits occur. This manual is sponsored by Defence Procurement Agency.



Passive Contaminant Control

- Complete avoidance of harmful chemicals
- Regulate introduction of materials
- Toxicological review of materials (INM)
- Materials toxicity manual
- Maintain vigilance onboard

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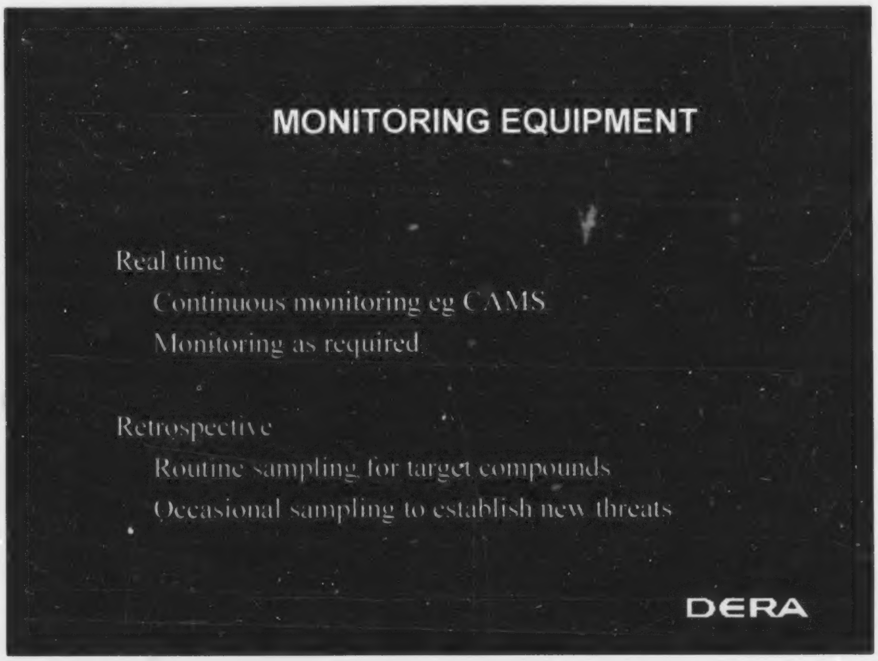
The ideal method of contaminant control is complete avoidance of the contaminating chemicals, but we live in a real world and so we need to regulate the materials which are required to be carried on board.

To that end INM Health & Hygiene Division conduct toxicological reviews of any new materials or equipment to be introduced into service. In co-operation with the manufacturers and the personnel who would use the product , an assessment is made as to what substances are contained, how they may escape from a material into the atmosphere and whether the material will be in contact with the atmosphere or sealed. A toxicological risk assessment is then conducted to decide whether the material may be approved for unrestricted use, may be restricted for use in specific circumstances only (e.g. must be cured fully before being placed onboard) or is totally banned from use.

The details of these materials are laid down in an RN document , the materials toxicity guide which is held onboard, and flagged up with the stores provision organisation. Shore personnel arranging maintenance and repair processes have a responsibility to inform contractors of the materials limitations and screen any materials to be used by contractors.

All personnel are required to maintain vigilance to keep the system functioning, and breakdowns in the system may be detected by changes in the profile of the retrospective analysis results.



MONITORING EQUIPMENT

Real time
- Continuous monitoring eg CAMS
- Monitoring as required

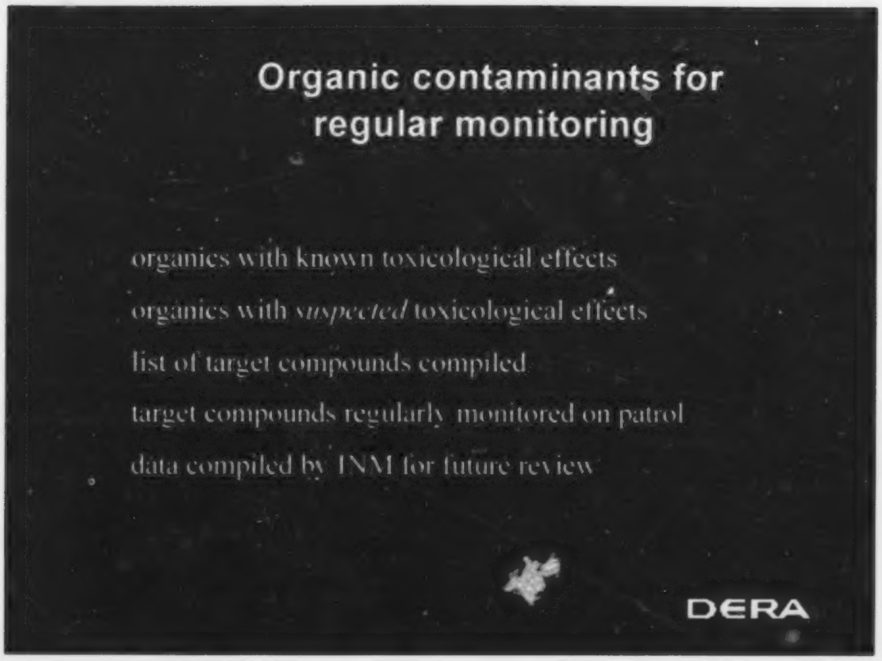
Retrospective
- Routine sampling for target compounds
- Occasional sampling to establish new threats

Modern equipment has now displaced the mice.

Akin to the US Navy real time continuous monitoring is carried out from fixed sampling points using a Central Atmosphere Monitoring System (CAMS), bases on a Mass Spectrometer with infra red analysis for CO. This is complemented by the use of single species portable monitors for a number of other contaminants of health concern. The next speaker will deal with these monitors in more detail.

All monitoring is recorded and then assessed by the submarine's Squadron before being forwarded to INM for entry into a computerised database which highlights MPC breaches and unusual trends, and is then stored for medico-legal purposes.

Retrospective monitoring method was required for the other contaminants and to meet the assessments of new threats.



Organic contaminants for regular monitoring

organics with known toxicological effects

organics with *suspected* toxicological effects

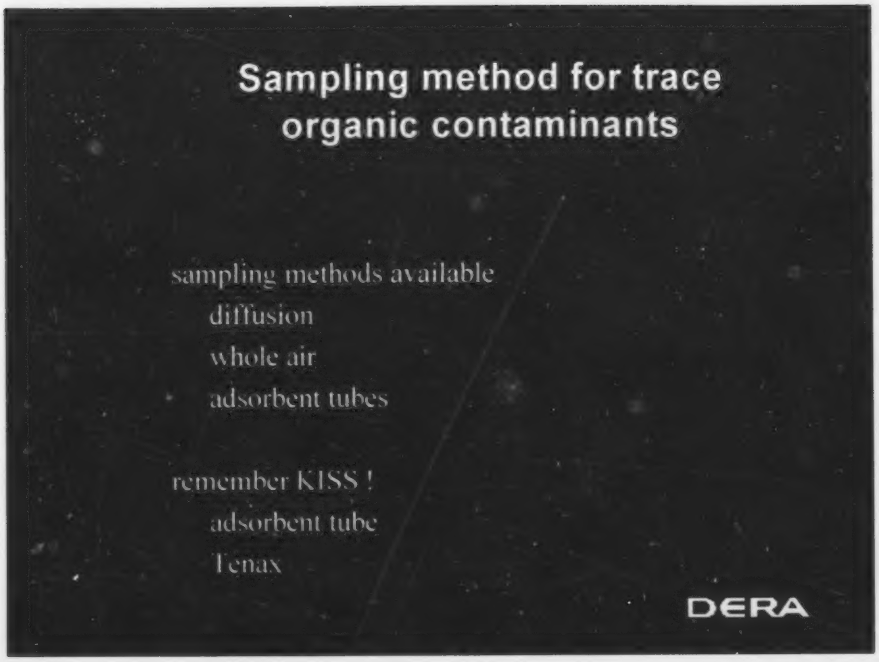
list of target compounds compiled

target compounds regularly monitored on patrol

data compiled by INM for future review

DERA

The discussion resulted in the selection of 30 compounds. Either known to have toxicological effects or suspected to have such effects. This then forms the list of compounds regularly monitored for. Details of all these analyses are retained for further reference and research.



Sampling method for trace organic contaminants

- sampling methods available
  - diffusion
  - whole air
  - adsorbent tubes
- remember KISS !
  - adsorbent tube
  - Tenax

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So we needed a method by which to *sample* these contaminants , 30 chemicals in the target list, which was suitable for use by submariners and which would be simple enough to use and give reliable, reproducible results.

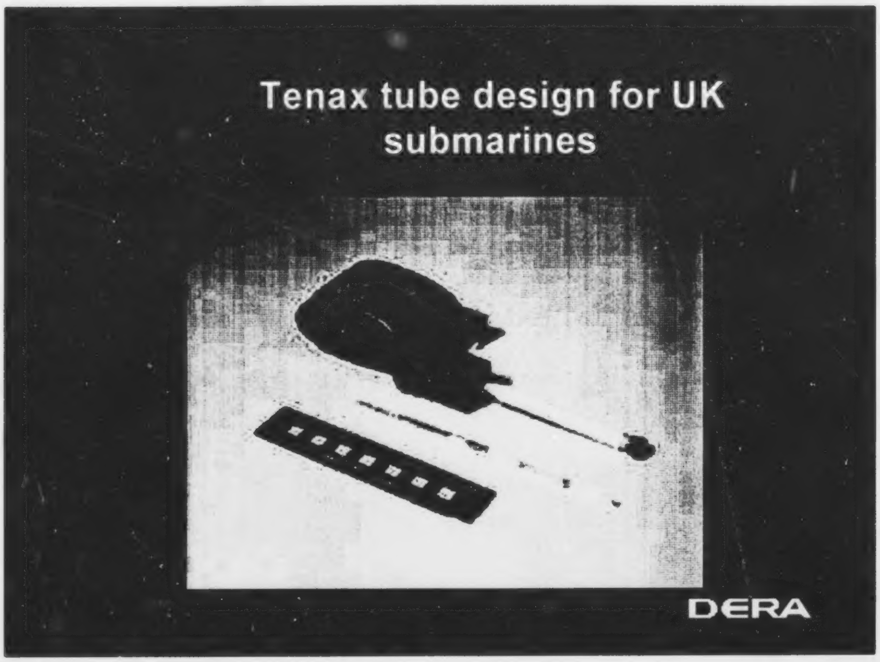
Of the sampling methods available at the time:

- diffusion tubes available were felt to be unsuitable to collect the targeted 30 compounds for quantitation since many of the diffusion coefficients needed for quantitation were unavailable.

- whole air sampling into evacuated electropolished stainless steel cylinders was attractive and simple to use, but too expensive as a monitoring system for issue to the whole submarine flotilla

- sampling into tubes containing an adsorbent was thought to be the simplest approach and it was suitable to preconcentrate the mixture of contaminants enabling us to achieve lower detection limits.

Under the KISS (Keep it simple stupid) principle we felt this was the approach most likely to succeed. Submariners were already familiar with using Draeger detector tubes and the method was similar. DERA designed a sample tube containing an adsorbent Tenax which was good for adsorbing and preconcentrating trace organic contaminants.



Tenax tube design for UK submarines

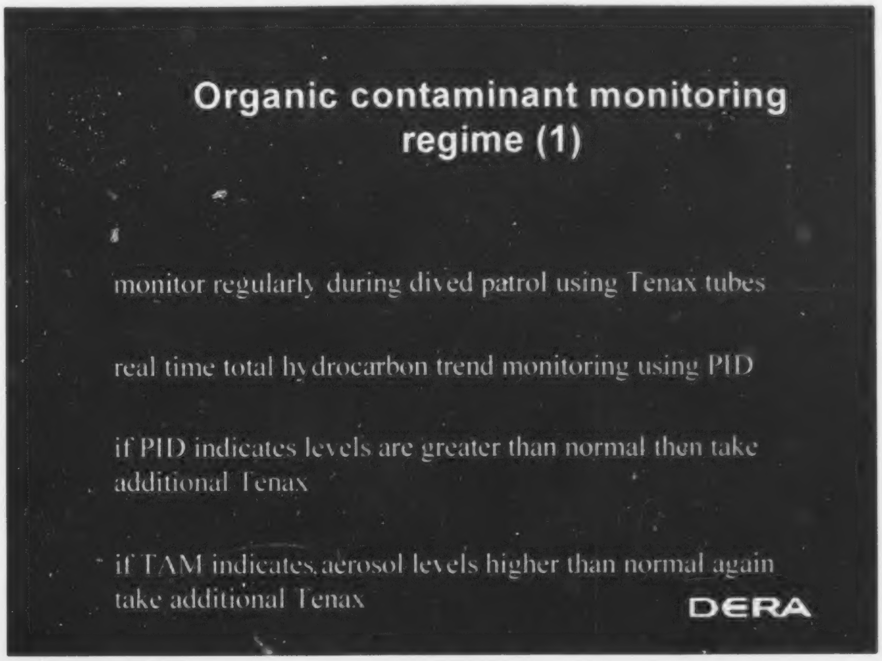
DERA

There were a number of adsorption tubes containing Tenax sold by various companies suitable if the sample is to be analysed within a few hours of taking the sample. The submarine samples could not be analysed for 3 months or so and so special tubes were needed to preserve the integrity of the samples.

The DERA team designed a glass tube of suitable dimensions to fit the analytical thermal desorption equipment and capable of being sealed after conditioning by fusing the glass ends.

The submarine air is sampled by drawing air through the Tenax adsorbent using a bellows pump and the tube then sealed immediately by sealing the glass tube ends with a hand held , commercial butane torch.

The tubes are then stored in the dark in boxes provided until the end of the patrol when they are returned to INM for analysis.



Organic contaminant monitoring regime (1)

- monitor regularly during dived patrol using Tenax tubes
- real time total hydrocarbon trend monitoring using PID
- if PID indicates levels are greater than normal then take additional Tenax
- if TAM indicates aerosol levels higher than normal again take additional Tenax

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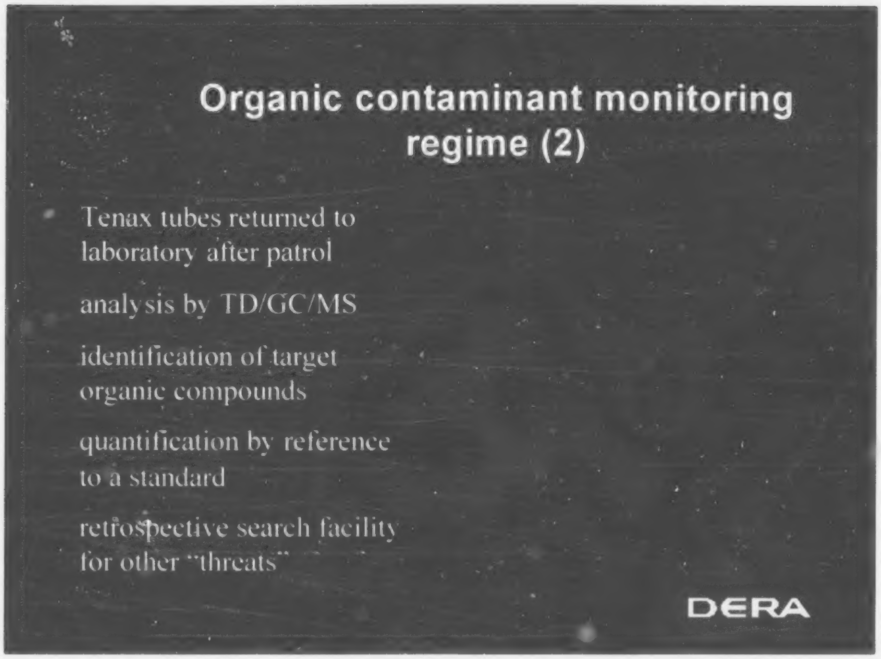
What is the sampling regime for these Tenax tubes ?

Boxes of prepared Tenax tubes are taken on patrol by each submarine with instructions to take samples at regular locations and times throughout patrol.

The submarines also carry a photoionisation detector to monitor real time TRENDS of hydrocarbon contamination . This portable PID (TOM) method is used for surveying various locations around the boat and if higher than "normal" concentrations of hydrocarbons are indicated ,then remedial action can be instigated and an additional Tenax tube sample can be taken for later assessment of the problem post patrol

Similarly a real time respirable aerosol monitor (TAM) is also embarked and is used to indicate when the aerosol levels are above "normal" and to take additional Tenax.



Organic contaminant monitoring regime (2)

- Tenax tubes returned to laboratory after patrol
- analysis by TD/GC/MS
- identification of target organic compounds
- quantification by reference to a standard
- retrospective search facility for other "threats"

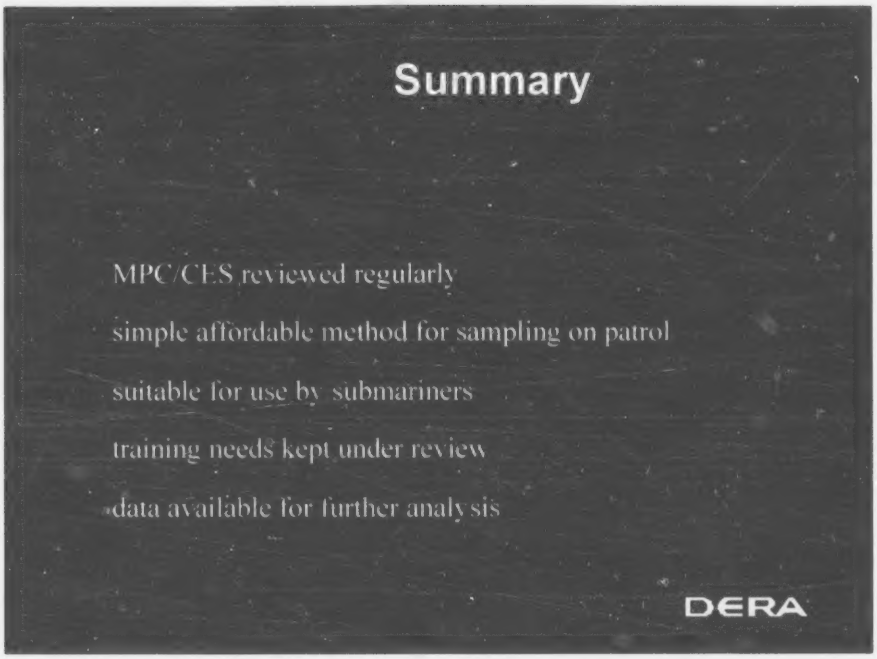
DERA

The Tenax tubes are returned to the routine laboratory at INM after patrol

- and the tubes are analysed by thermally desorbing the contaminants (TD) separating them by gas chromatography (GC) and identifying and quantifying them by mass spectrometry (MS) with reference to an internal standard.

The submarine ambient concentrations of the target 30 contaminants are collected in a database at INM for scrutiny by MOSM and the CO of the submarine is also informed.

The mass spectrometric data stored magnetically, can also be used for a retrospective search for other contaminant compounds which may have become a matter for concern or for new threats to atmosphere quality.



Summary

MPC/CES reviewed regularly

simple affordable method for sampling on patrol

suitable for use by submariners

training needs kept under review

data available for further analysis

DERA

In conclusion then:

- we have a simple, affordable method of sampling for trace contaminants which we know to be present in submarine air and about which we have health concerns which is usable by

- method of sampling is suitable for use by non scientific personnel.

- the exposure limits are reviewed regularly

- INM keep the training needs for this and other monitoring techniques under regular review

- the need to maintain records of these target compounds has been met

- a review of the inventory of Volatile Organic Compound contaminants has been constructed to allow new threats to air quality to be considered for inclusion in the target list. DERA are currently reviewing the methods of sampling and analysis to take account of contaminants which have become of recent concern eg aldehydes and siloxanes

SAMAP 2000

Third International Workshop

on

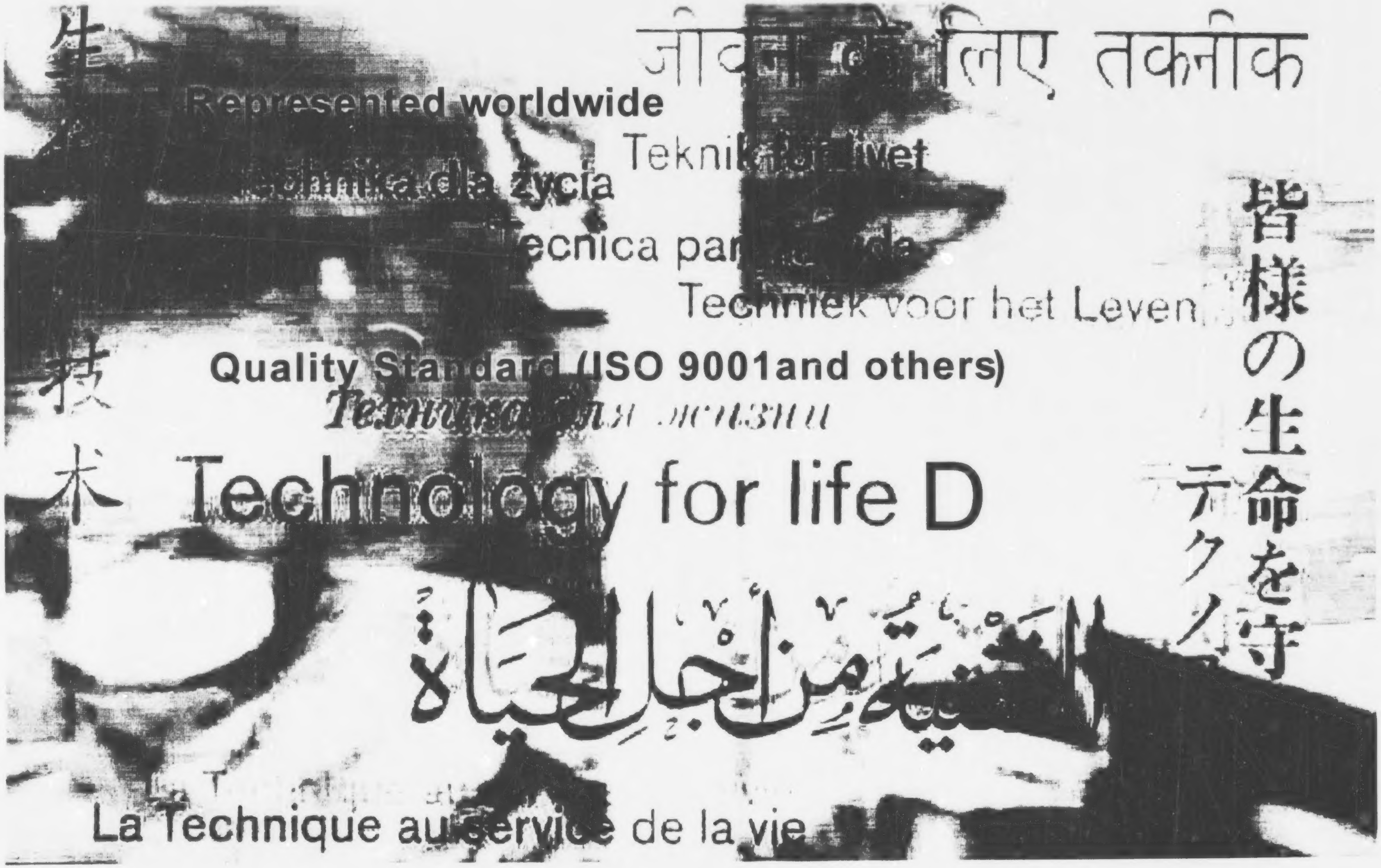
Submarine Air Monitoring and Air Purification

October 11th - 13th 2000

TORONTO

Steffen Kah/Dietmar Diercks
Breathing Gas Systems
Draeger Sicherheitstechnik GmbH
Germany

Rohan Fernando
Diving & Air Systems
Draeger Safety Inc
USA



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Technika dla życia

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Techniek voor het Leven

皆様の生命を守

テクノ

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Техника для жизни

生 技 术

Technology for life D

التقنية من أجل الحياة

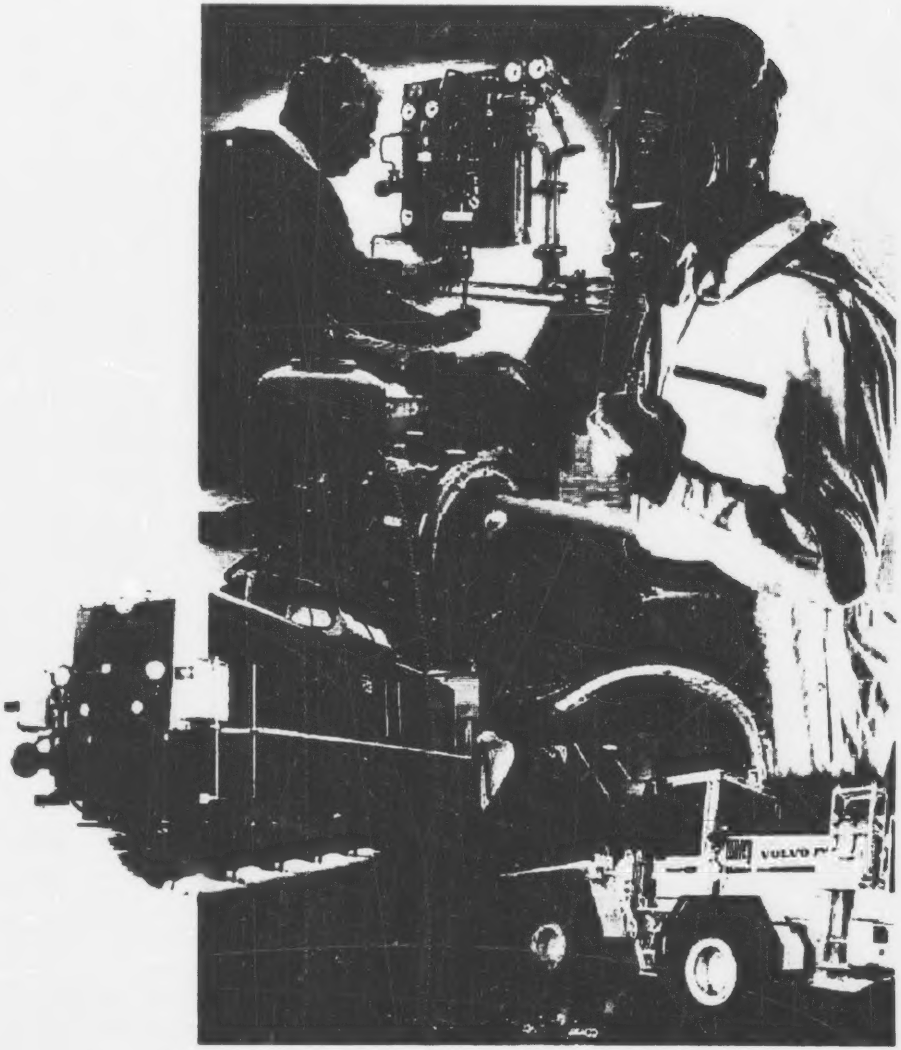
La Technique au service de la vie

Business Unit

BreathingGas Systems

System solutions for safe breathing in special applications

...manages Submarine Systems



Submarine Air Management and Monitoring System

The new system under development by Draeger consists of

•a modular air management system and

•a new air monitoring system

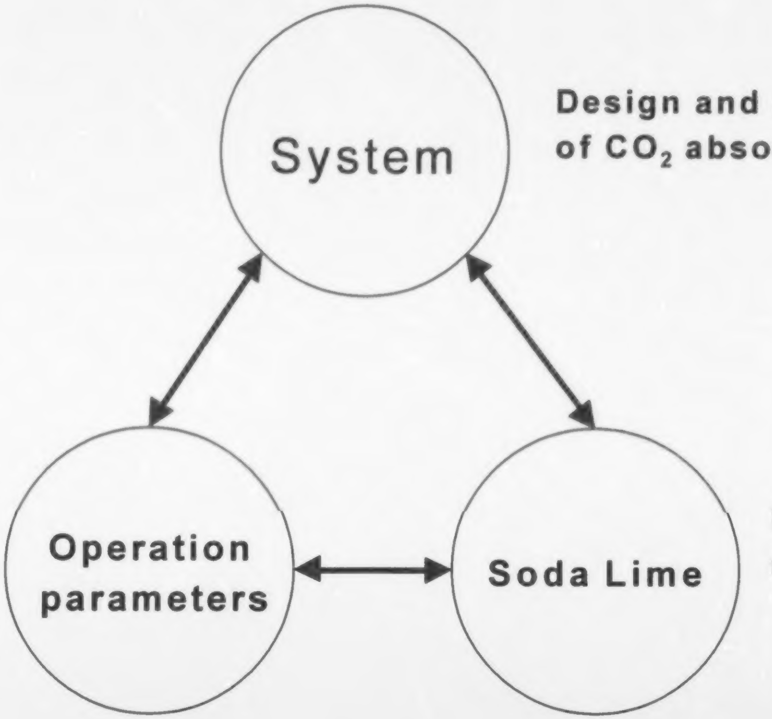
Air management system development involves

- **Optimisation of the carbon dioxide absorption system**
- **Development of a toxic gas absorber**
- **Design of a modular system adaptable for different submarines**

Monitoring system development

- **based on the IMS principle proven in other GD applications**

Development program
Optimization of Carbon Dioxide Absorption System



System

Design and development
of CO_2 absorber

Operation parameters

Research for
optimisation

Soda Lime

Improvement of
soda lime performance

Results of development program

- New Dräger soda lime DiveSorb S fulfils the requirements
- Performance of Dräger cartridge CH 16720 has been improved and still suitable for all Dräger scrubbers
- Flow rate was a decisive parameter in optimising absorbing capacity
- The cartridges perform best in parallel arrangement
- The optimal quantity of cartridges per module is 6
- Humidifying increases absorbing capacity when relative humidity of the ambient air is below 60 %

Carbon Dioxide Absorber

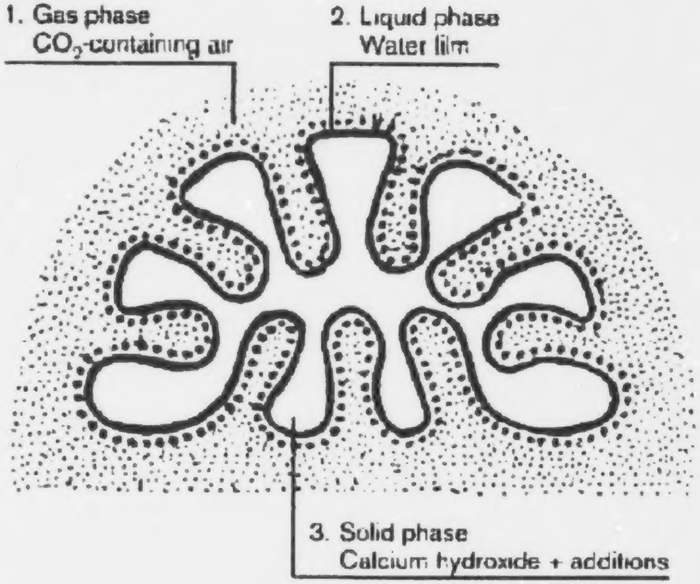
Shape: Hemispherical pellet

Colour: White

Size: Diameter: approx.. 4 mm

Tyler Mesh: 5 - 9

DIN 4188: 2 - 4 mm


1. Gas phase
CO_2-containing air
2. Liquid phase
Water film
3. Solid phase
Calcium hydroxide + additions

Soda lime cartridge CH 16720

Dräger
Dräger

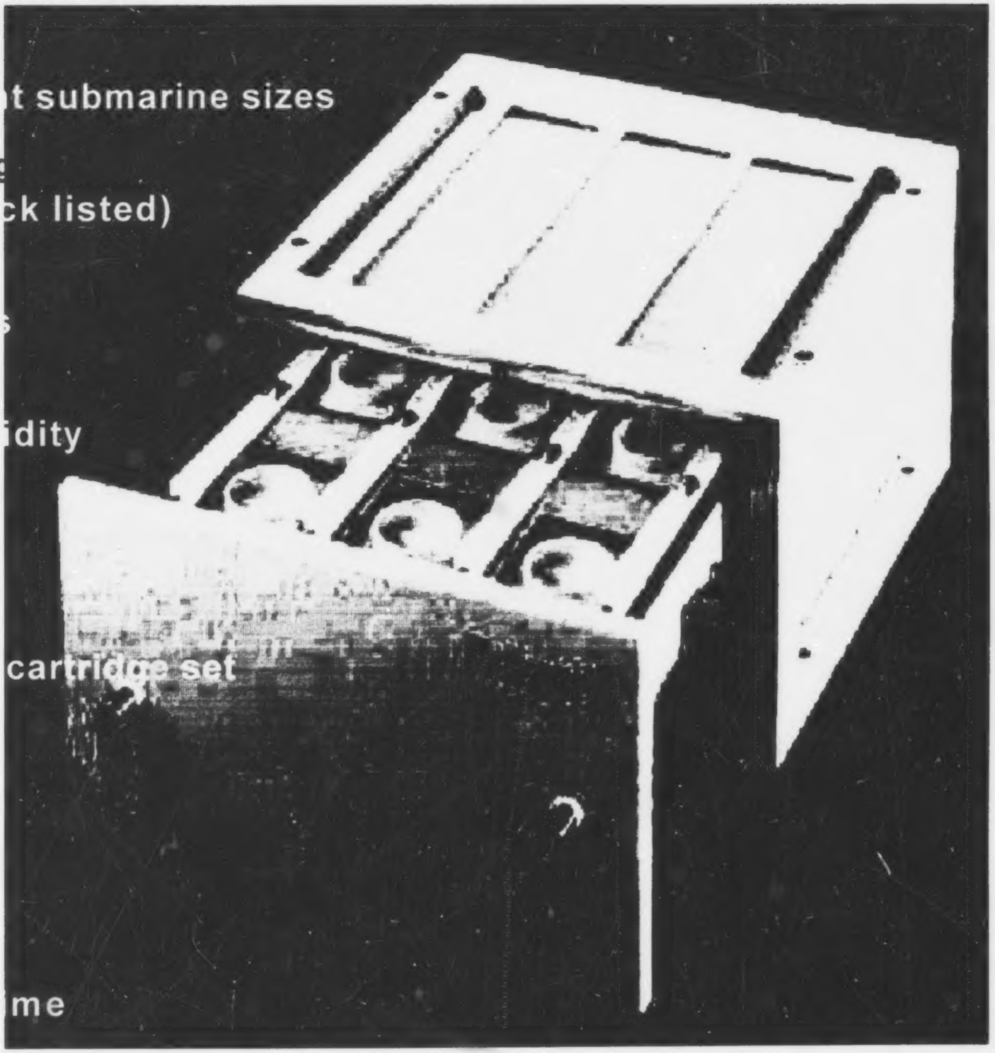
Weight: 4.7 kg

Dimensions: 204x 234x 134 mm (L x H x D)

Composition: Calcium Hydroxide, Water, Sodium Hydroxide

Water content: 21 ± 2%

Carbon Dioxide Absorption Module



- Module design

t submarine sizes

- Use of existing Dräger cartridg

ck listed)

- Shock resistance

s

- Ambient operating conditions

idity

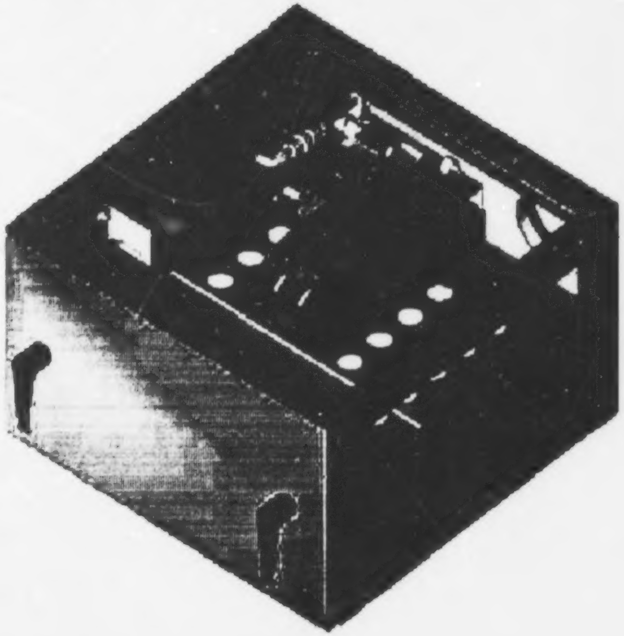
- Flow rate
- Operation time

cartridge set

- Pressure drop
- Carbon dioxide level
- Absorbing capacity

me

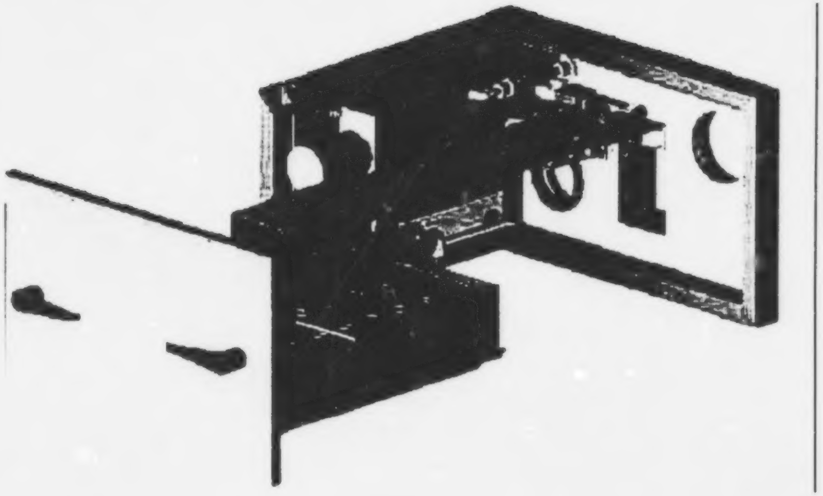
Humidifier Module



- •Nominal flow rate
  - 120 m3/h
  - *generating….*
- •Humidity of
  - up to 80% RH at 20°C
- •Pressure drop
  - below 1000 Pa (10mbar)

Performance of soda lime improved by humidifying… ….

- •Modular design
  - same rack dimensions
- •Placement
  - Upstream of CO_2 module

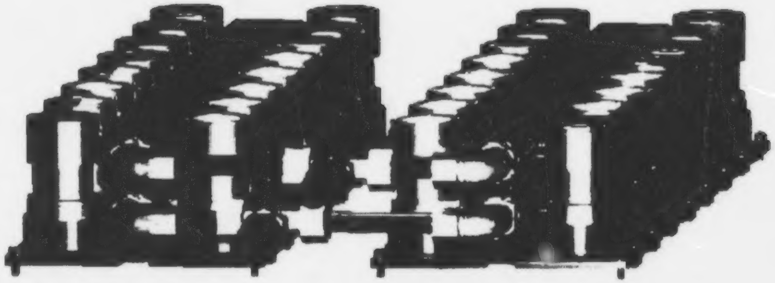


Humidifier Module

Operating Principle

Polysulphone hollow fibres are fed with warm water (min. 60°C) from an external source. Distilled water highly recommended

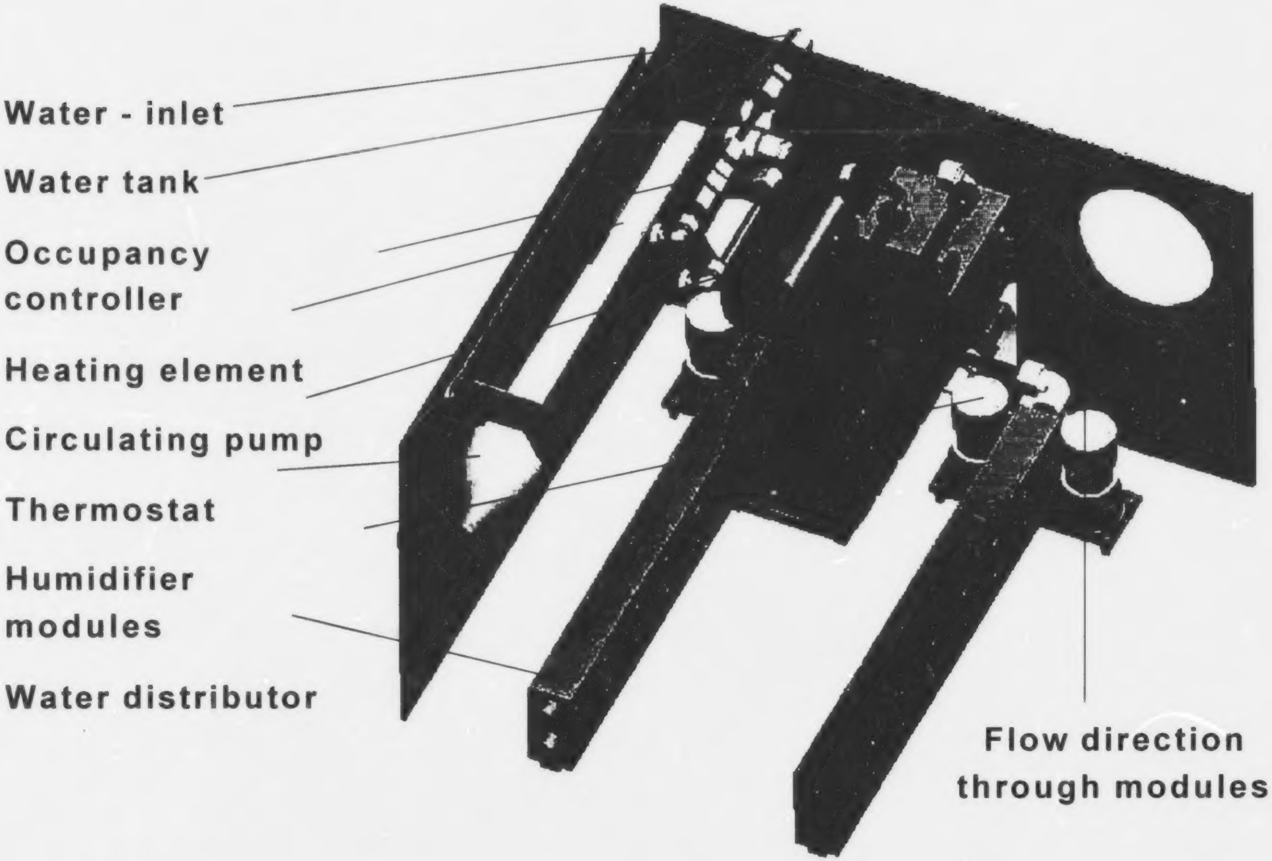
- Intake air to be humidified passes internally through the fibres. Intake air must be dust free
- Water vapour passes over the fibre membranes due to the lower partial pressure compared with that of the warm water



- No additional power required when warm water is available
- Integrated heater maybe installed for cold water systems or as a booster

Humidifier Module

Component details


Water - inlet
Water tank
Occupancy controller
Heating element
Circulating pump
Thermostat
Humidifier modules
Water distributor
Flow direction through modules

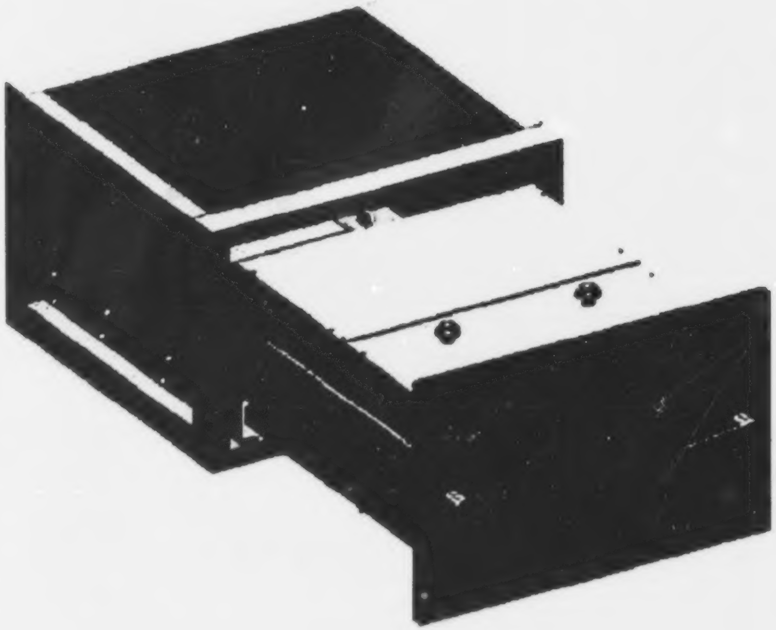
Air Purification Module

A relatively new task of air purification in submarines is

>to remove the substances not generated by human breathing

>and which cannot be absorbed with soda lime

>development of an Air purification Module

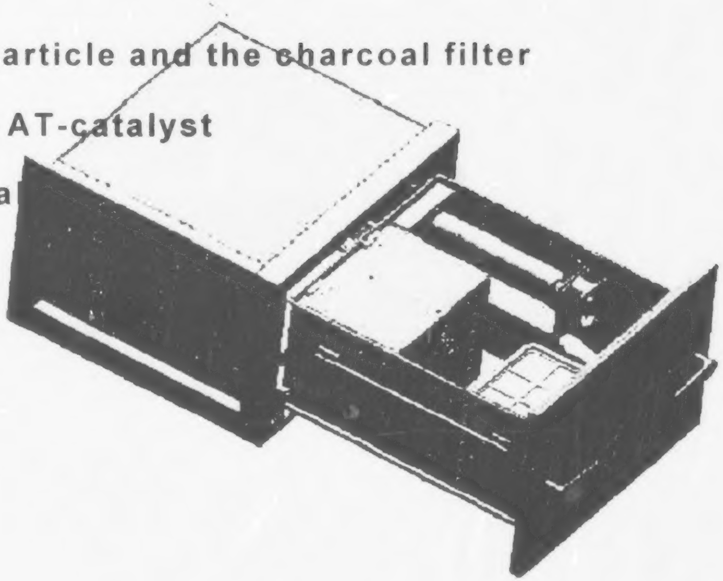


- Modular design
  - same rack dimensions
- Placement
  - Parallel to CO_2 absorption & humidifier modules

Air Purification Module

consists of…..

- a high efficiency particle filter
- an activated charcoal filter
- an Ambient Temperature (AT)-catalyst with Palladium-Platinum
- a High Temperature (HT)-catalyst with Palladium in an aluminium structure

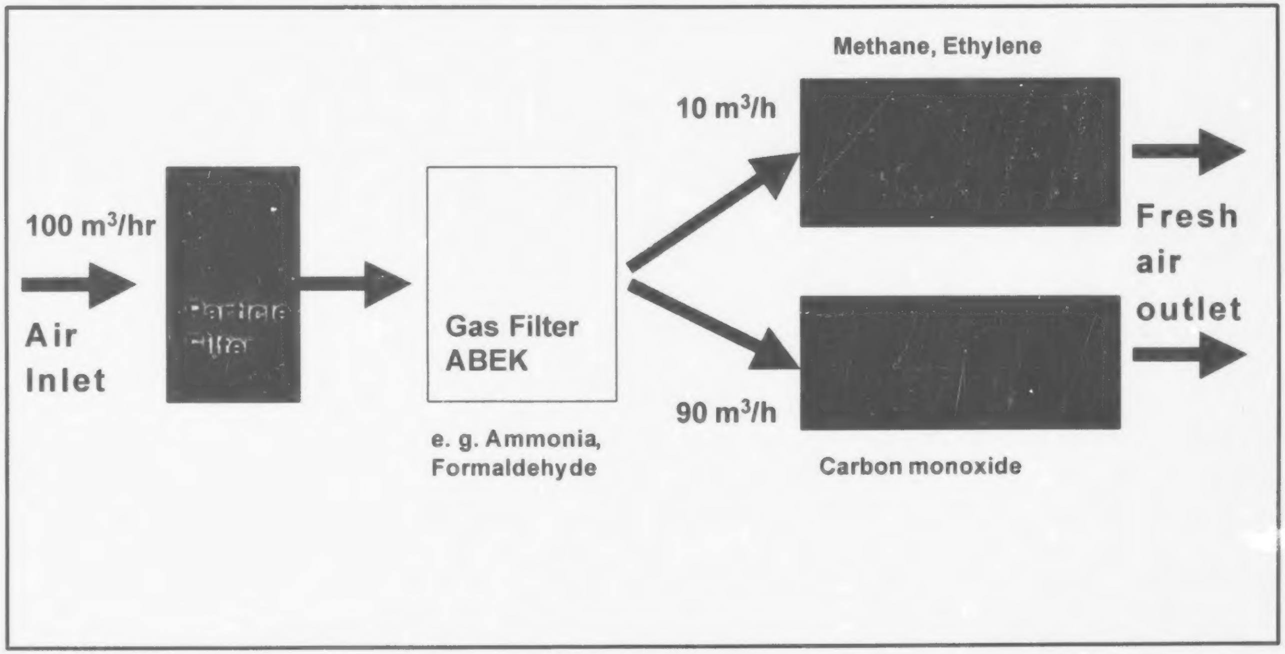


- **Most substances are collected in both the particle and the charcoal filter**
- **CO will be modified to CO_2 and water in the AT-catalyst**
- **Ethylene and Methane treated in the HT-cata**

Module parameters:

- **100 m^3/h air intake**
- **Max. pressure drop 1000 Pa**

Air Purification Module



100 m³/hr

Air Inlet

Particle Filter

Gas Filter ABEK

e. g. Ammonia, Formaldehyde

10 m³/h

90 m³/h

Methane, Ethylene

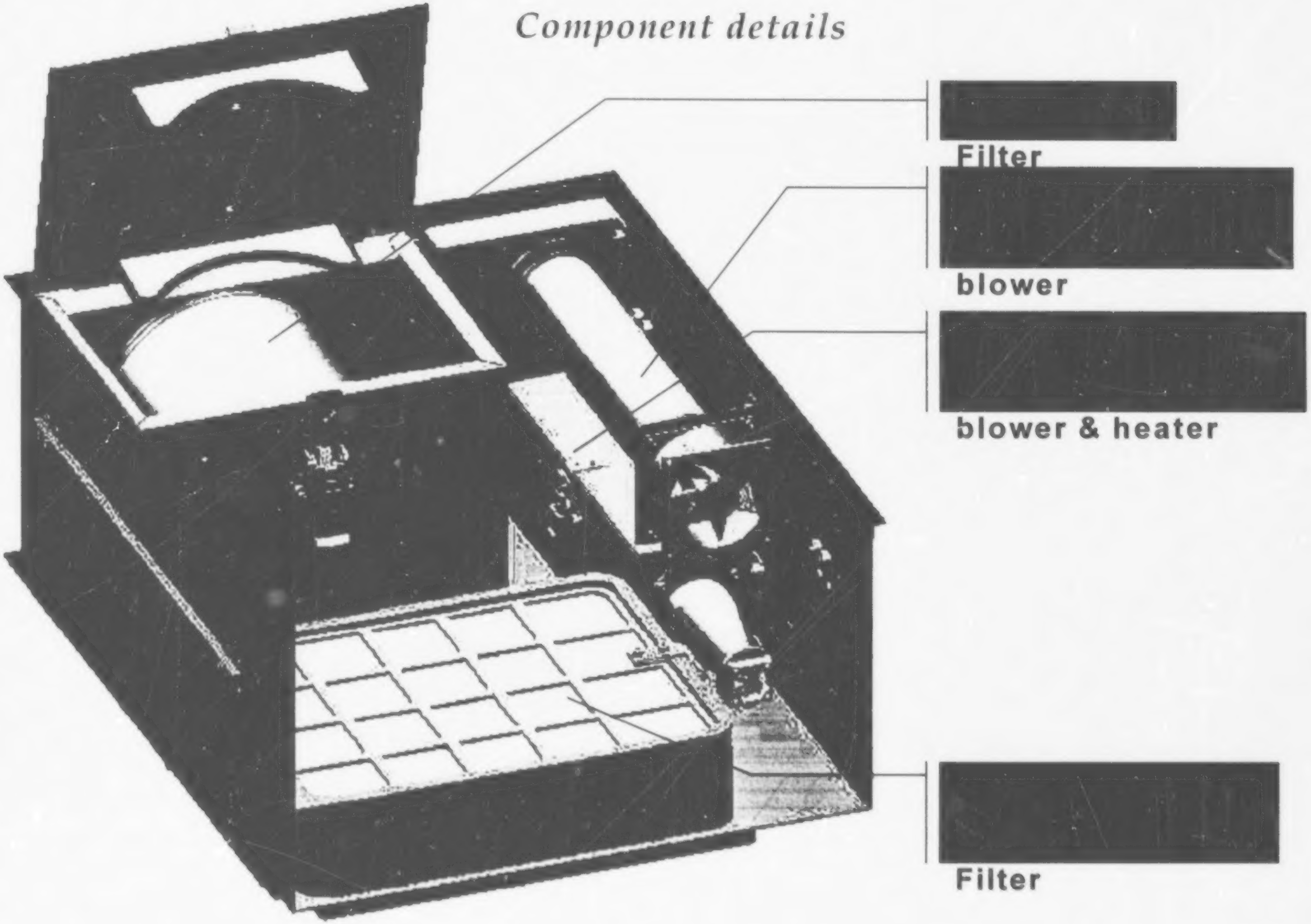
Carbon monoxide

Fresh air outlet

Block diagram- Module component arrangement

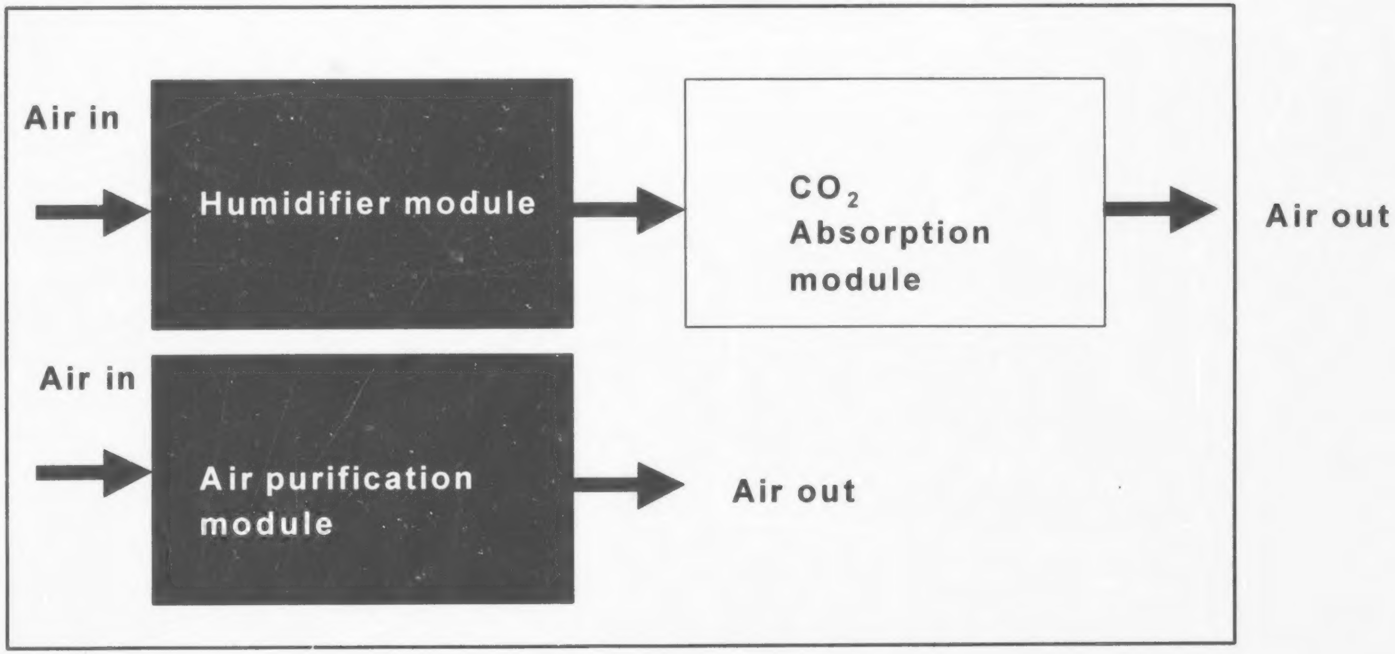
Air Purification Module

Component details


Filter
blower
blower & heater
Filter

AIR FLOW

- *directed in series through Humidifier & CO2 Absorption modules*
- *directed in parallel through the Air Purification modules*



Air in

Humidifier module

CO_2 Absorption module

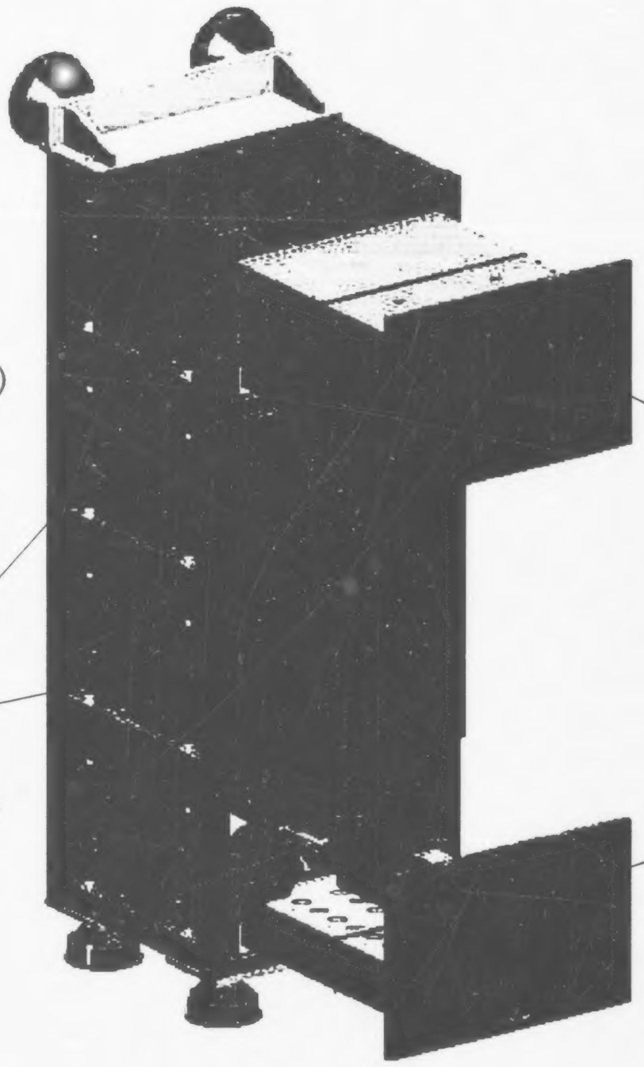
Air out

Air in

Air purification module

Air out

Submarine Air Management System (e.g. Recommendation for 30 man submarine)


Air purification module
carbon dioxide absorbtion modules
Humidifier module

Air Monitoring System

ION MOBILITY SPECTROMETER offers

Real Time Analysis Techniques
Quantitative and Qualitative Analysis in ranges of ppb-low ppm

Application of IMS in Submarine air sampling

- Preliminary stage
- Examining existing Draeger systems in Gas Detection

AMINE REGENERATIVE SCRUBBER PILOT PLANT PERFORMANCE TESTS.

Effects of carbon dioxide loading, temperature and humidity during fifteen hundred hours of scrubbing.

David Eaton, M.Sc., P.Eng.
Defence and Civil Institute of Environmental Medicine

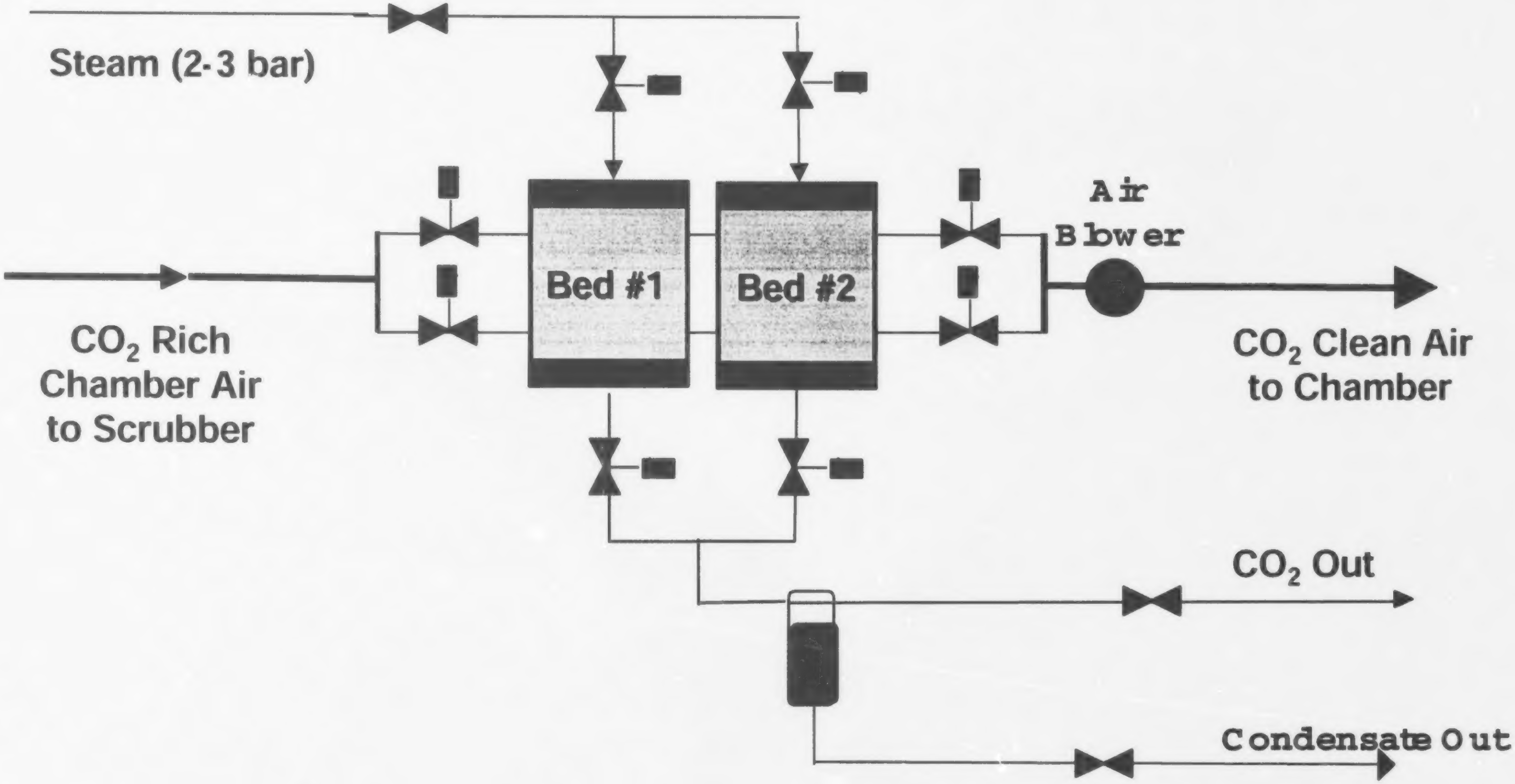
National Defence Défense nationale

Canada

Programme

- The scrubber,
- the experiments,
- the results,
- the conclusions.

The Scrubber (Schematic)



Steam (2-3 bar)

CO_2 Rich
Chamber Air
to Scrubber

Bed #1

Bed #2

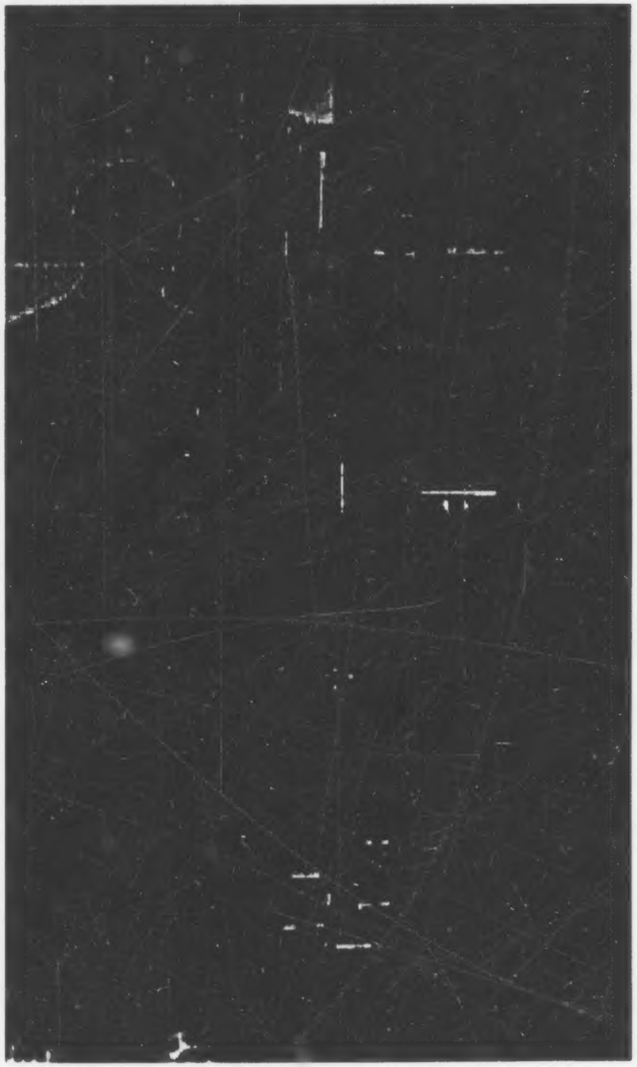
Air
Blower

CO_2 Clean Air
to Chamber

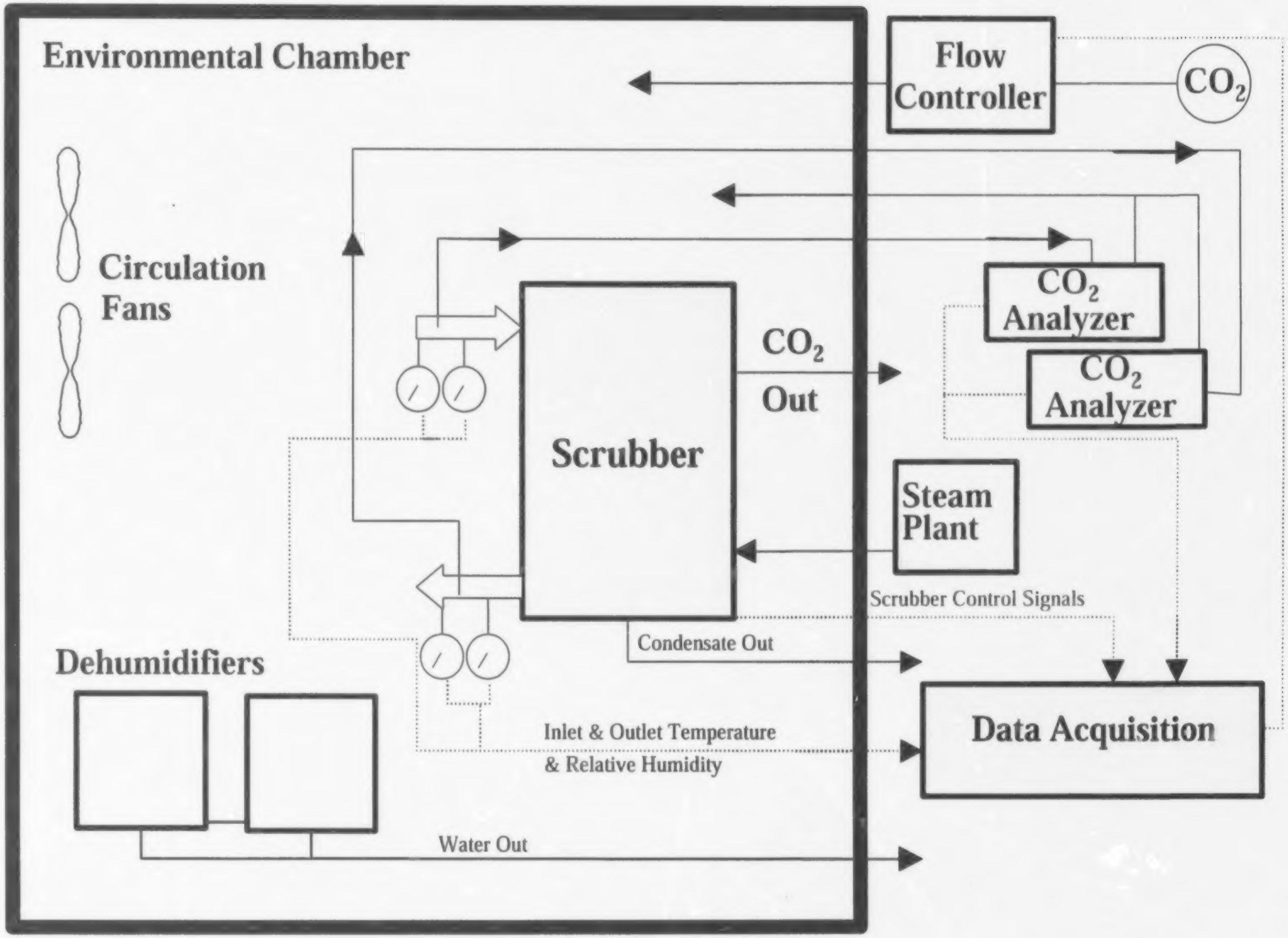
CO_2 Out

Condensate Out

The Scrubber (Physical)



Experimental Setup



Environmental Chamber

Circulation Fans

Dehumidifiers

Scrubber

CO_2 Out

Condensate Out

Inlet & Outlet Temperature & Relative Humidity

Water Out

Flow Controller

CO_2

CO_2 Analyzer

CO_2 Analyzer

Steam Plant

Scrubber Control Signals

Data Acquisition

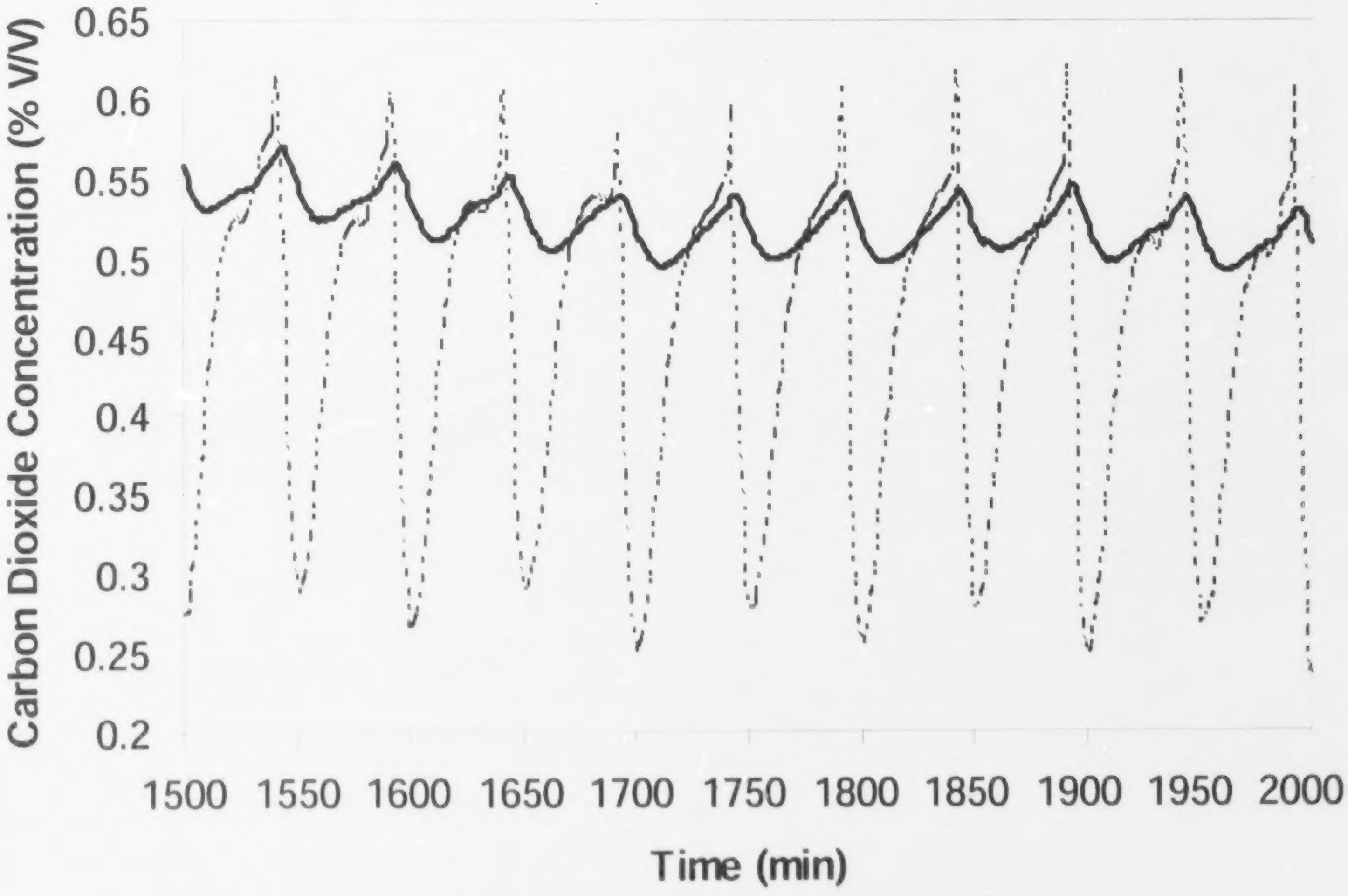
Experiments

- Reliability over 1500 h of operation
- carbon dioxide adsorption capacity
  - CO_2 loading for $[CO_2]_{chamber} = 0.5\%$
- effects of:
  - carbon dioxide loading
  - temperature
  - humidity
  - 2^n factorial

Factors and levels

	LOW	HIGH
CO_2 Load (# people) *(one person = 0.4 lpm)*	1	90% of capacity
Temperature (°C)	10	30
Relative Humidity (%)	50	100

Sample Data


Carbon Dioxide Concentration (% V/V)
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
1500
1550
1600
1650
1700
1750
1800
1850
1900
1950
2000
Time (min)

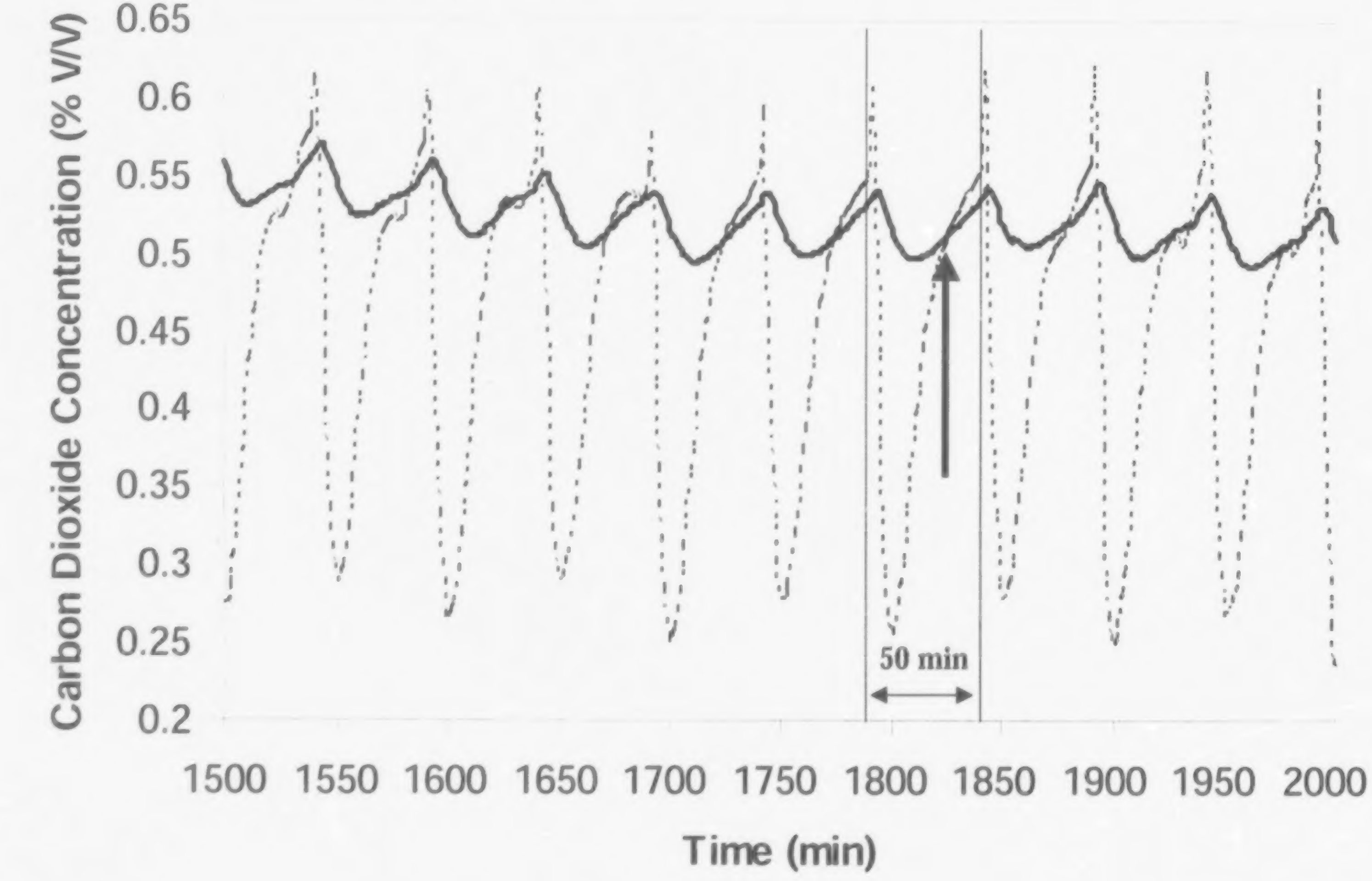
Results (Endurance)

- Completed >1500 hours
  - 1497 under observation
  - >5 h during commissioning
- one failure of the scrubber
  - temperature safety failed in Bed #2
  - prevented steam desorption
  - sensor shorted out and experiment continued
- longest continuous operation: 1272 hours

Results (Capacity)

- 50 minute adsorption time
  - 3.5 persons

Adsorption vs Regeneration Time



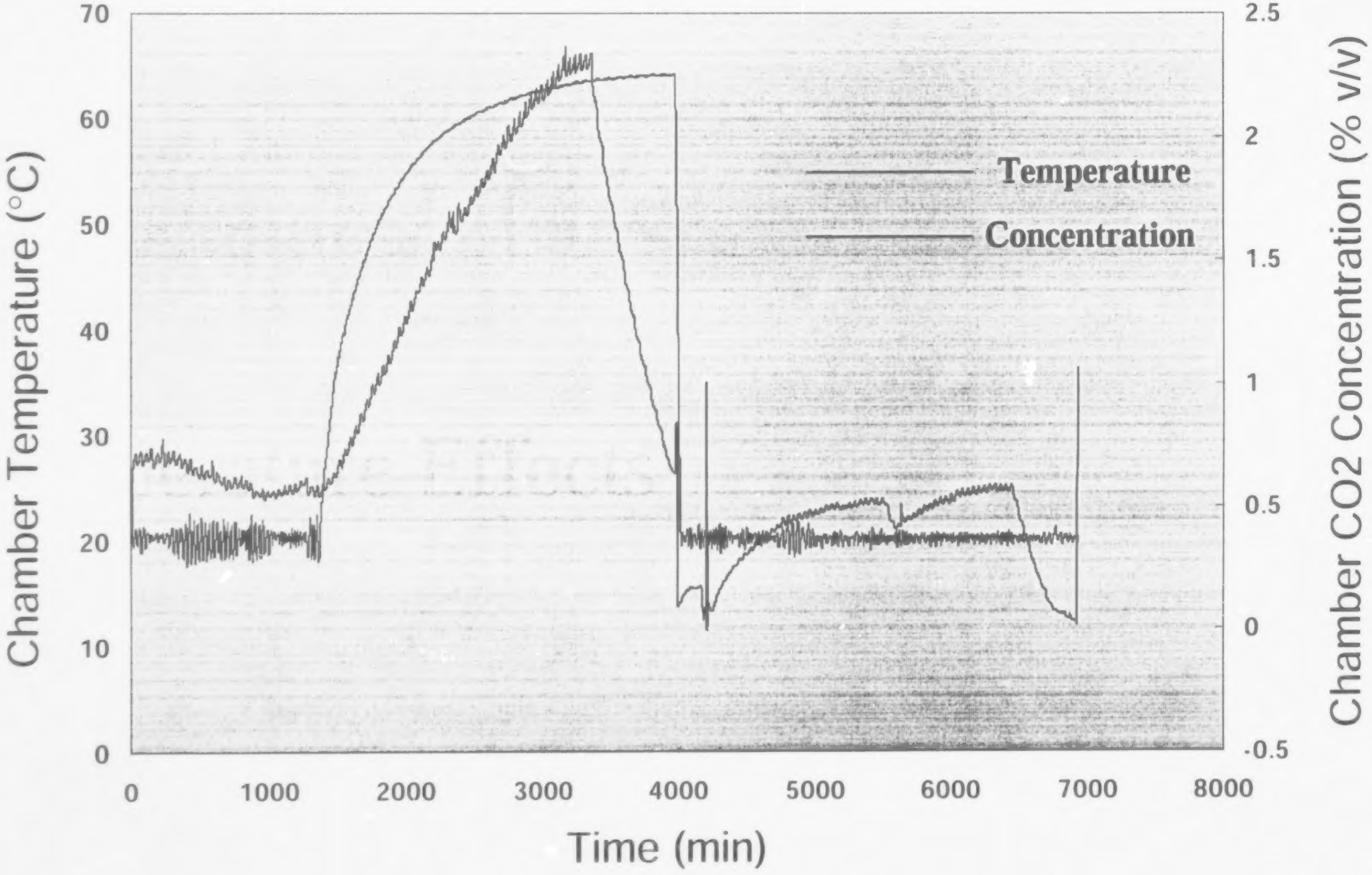
Results (Capacity)

- 40 minute adsorption time
  - 4 persons
  - matches Astrium design

Results (Factorial)

- Effects on Chamber Carbon Dioxide Concentration
  - carbon dioxide injection rate (ANOVA, $p = 0.047$)
  - relative humidity (no detectable effect)
    - low (54 - 76% R.H.)
    - high (84 - 85% R.H.)
  - chamber temperature (ANOVA, $p = 0.101$)

Temperature Effects



Other Investigations

- CO_2 ejected
  - quantity and purity
  - comparison to CO_2 loading
- effects of temperature, humidity, CO_2 loading and desorption bed on:
  - efficiency
  - desorption time
  - bed temperature

Conclusions

- Reliability
  - 1500 h possible with minimal downtime
  - *even in a pilot plant*
- chamber CO_2 concentration
  - positively correlated to CO_2 loading and temperature
  - no relative humidity effect detected
- adsorption capacity
  - measured was equal to or slightly greater than design
  - suggests mature technology suitable for full-scale design

Questions?

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1133 Sheppard Ave., West,
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Canada M3M 3B9

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E-mail: Dave.Eaton@dciem.dnd.ca

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Defence and Civil Inst of Environmental Medicine, Downsview ONT (CAN);Humansystems Inc, Guelph ONT (CAN)
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Human-Machine Interface Considerations for Inclusion of an Electronic Map in a Mission System PDF File
McFadden, S.M.;Donderi, D.C.
Defence and Civil Inst of Environmental Medicine, Downsview ONT (CAN)
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Estimation of Towed Array Curvature PDF File
Dosso, S.E.;Collison, N.E.
Defence Research Establishment Atlantic, Dartmouth NS (CAN);Victoria Univ, Victoria BC (CAN) Centre for Earth and Ocean Research
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Physiological Responses of Exercised-Fatigued Individuals Exposed to Wet-Cold Conditions PDF File
Tikuisis, P.;Ducharme, M.B.;Moroz, D.;Jacobs, I.
Defence and Civil Inst of Environmental Medicine, Downsview ONT (CAN)
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Development of Firesafe Electrical Cable for Shipboard Use: Phase VIII PDF File
Murthy, M.K.;Das Gupta, S.;Johar, S.
Defence Research Establishment Atlantic, Dartmouth NS (CAN);Electrofeul Manufacturing Co Ltd, Toronto ONT (CAN)
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The Development of a New Format for the Canadian Department of National Defence Statement of Operational Requirement (SOR) PDF File
Greenley, M.P.
Defence and Civil Inst of Environmental Medicine, Downsview ONT (CAN);Humansystems Inc, Guelph ONT (CAN)
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Greenley, M.
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Review of Commercial HFE Standards and Guidelines PDF File
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National Défense
Defence nationale

Canada

Categorisation of Substances found in Submarine Atmospheres

Peter Evans
Sea Technology Group
UK MoD

DPA

SAMAP 2000 TORONTO

Why Categorise? - 1

- Many Substances
- Health
- Levels of Hazard
- Economy of Effort

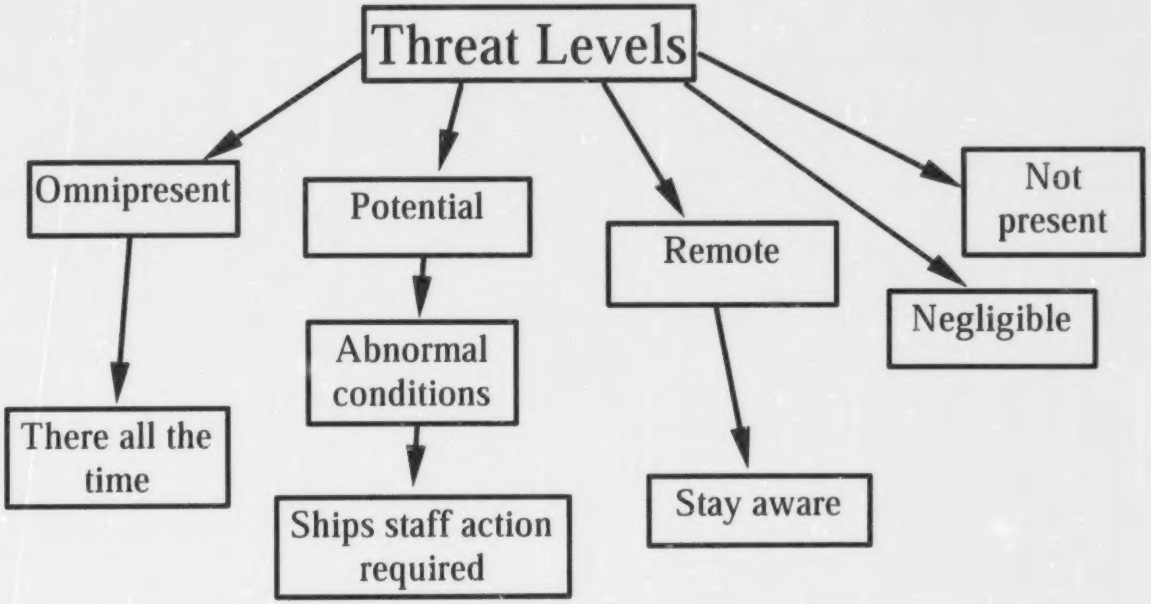
Why Categorise? - 2

- to *control* the atmosphere
- need to *measure* atmosphere
- for which *instrumentation* is required
- question is: *what* instrumentation?

The Thought Process

- General Linkage
  - level of hazard
  - “thoroughness” of monitoring
- Risk drives Monitoring

Hazards and Threats



Threat Levels

Omnipresent

There all the time

Potential

Abnormal conditions

Ships staff action required

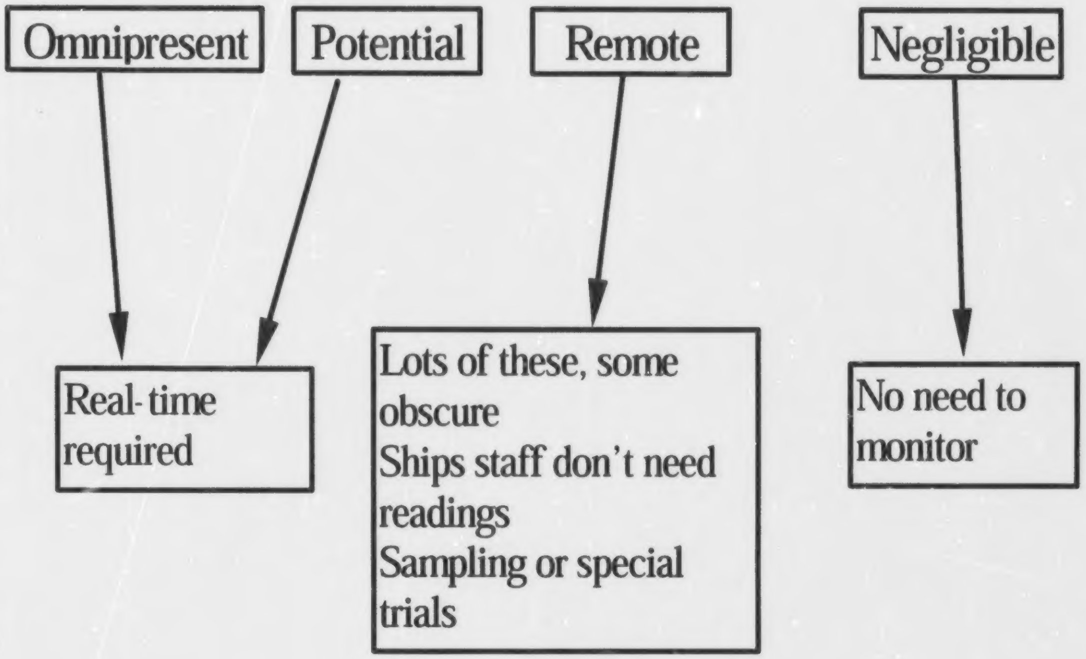
Remote

Stay aware

Negligible

Not present

General Monitoring Needs



Omnipresent

Potential

Remote

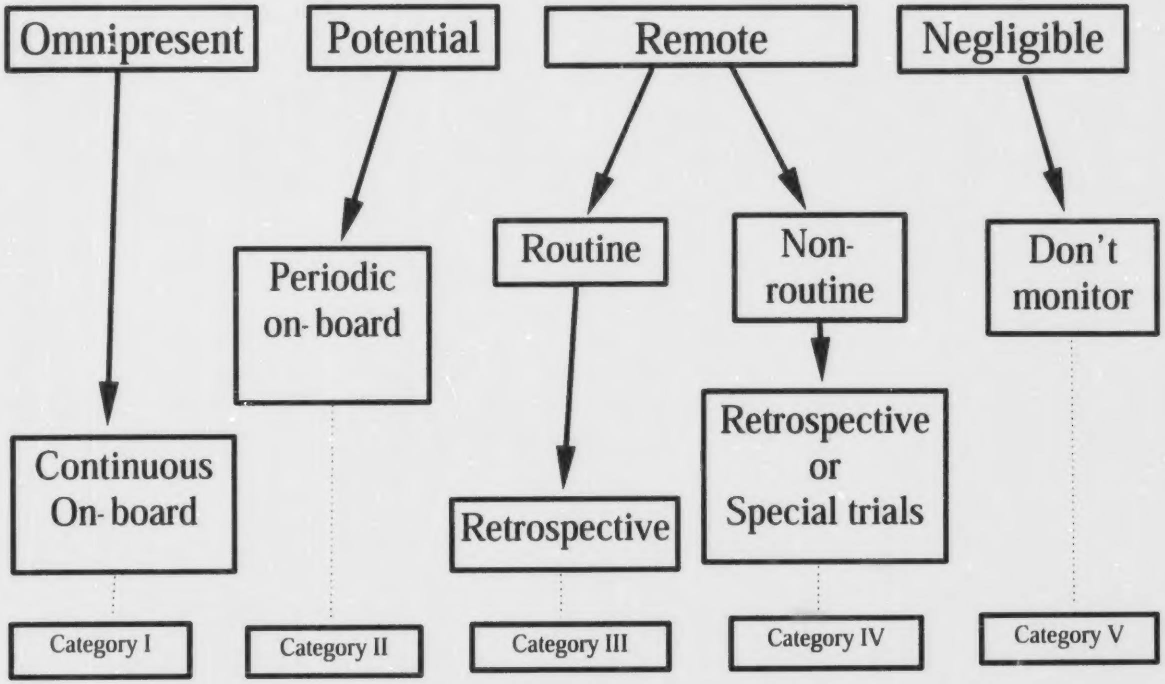
Negligible

Real-time required

Lots of these, some obscure
Ships staff don't need readings
Sampling or special trials

No need to monitor

Specific Monitoring Needs



Omnipresent → Continuous On-board ··· Category I

Potential → Periodic on-board ··· Category II

Remote → Routine → Retrospective ··· Category III

Remote → Non-routine → Retrospective or Special trials ··· Category IV

Negligible → Don't monitor ··· Category V

DPA

Category I Described

- Life gases or Major contaminants
- Hazard level:
  - *Omnipresent*
- Monitoring Requirement :
  - *Continuous real- time*

Category II Described

- Hazard only in abnormal conditions
- Ships staff action required
- Hazard level: *Potential*
- Monitoring : *Periodic real-time*

Category III Described

- Immediate threat unlikely
- Health effects not negligible
- Regular account required
- Justifies ships staff sampling
- Hazard: *Remote, but still significant*
- Monitoring: *Routine retrospective*

Category IV Described

- No serious hazard
- Worth keeping track of
- Hazard : *Remote, but not negligible*
- Monitoring : *Non-routine retrospective, or special trials*

Category V Described

- Written off as potential threats
- Various reasons
- Hazard level: *Negligible*
- Monitoring Requirement : *Not monitored*

The Categorisation Process

- Team:
  - medical, toxicity, engineering, purification, monitoring, materials, safety
- List of substances
- Scrutinise - categorise
- Hard cases - structured, risk based process

Risk Assessment

- Records
- Risk analysis
- Risk assessment
- “Must haves”:
  - permissible concentrations
  - operating experience
  - expertise

The Outcome

• Category I	8%
• Category II	11%
• Category III	26%
• Category IV	34%
• Category V	21%

Using the Categories

- Category I : (Benzene)
- Category II : Weapon propellant
- Category III : Toluene
- Category IV : Methyl Chloride
- Category V : Phosphine, Acetic acid

Conclusions

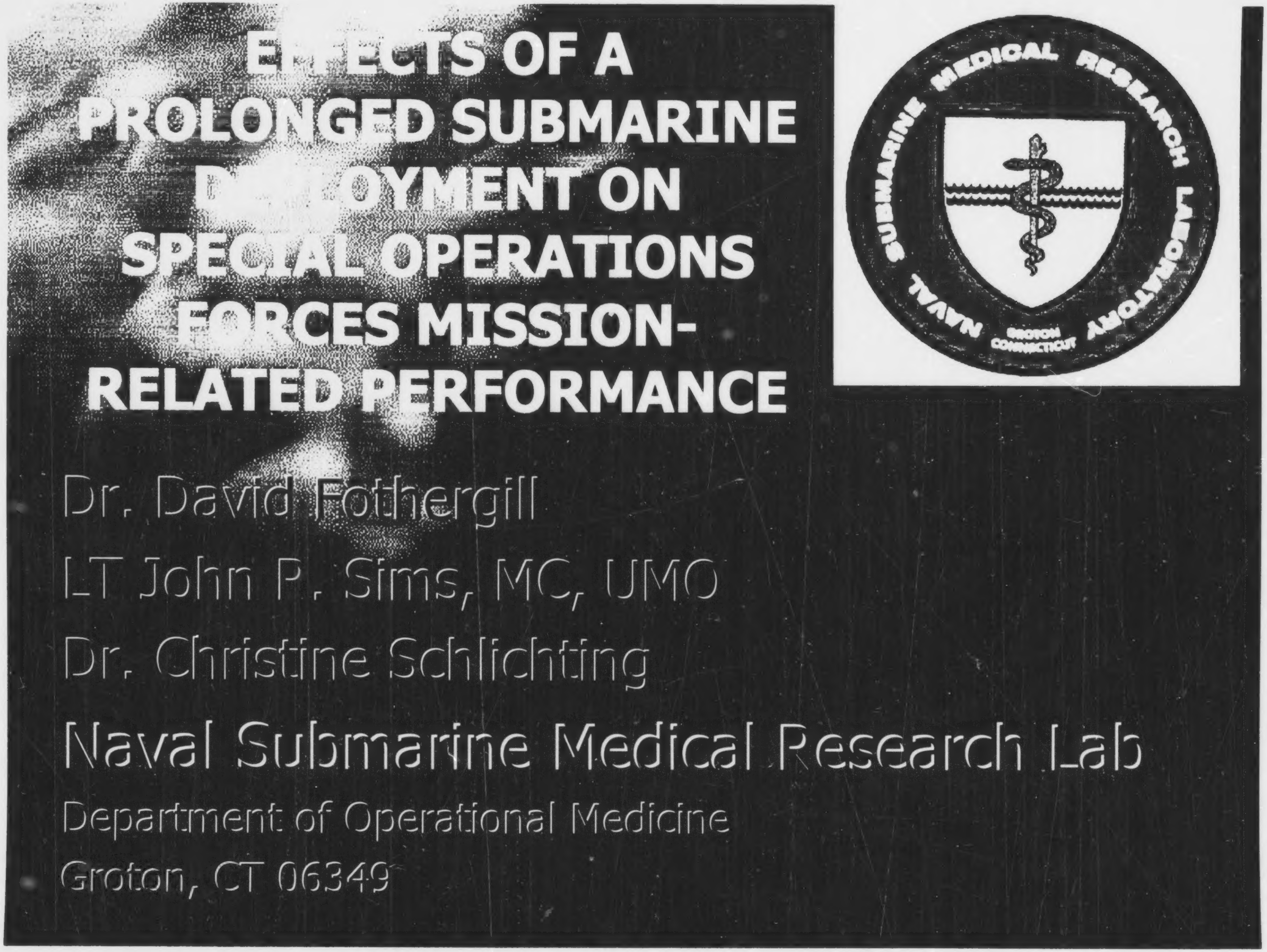
- Rational basis
- Manageable, practicable, general support
- Straightforward
- Risk assessment based
- Useful guide to priorities

The Last Word

It's a framework

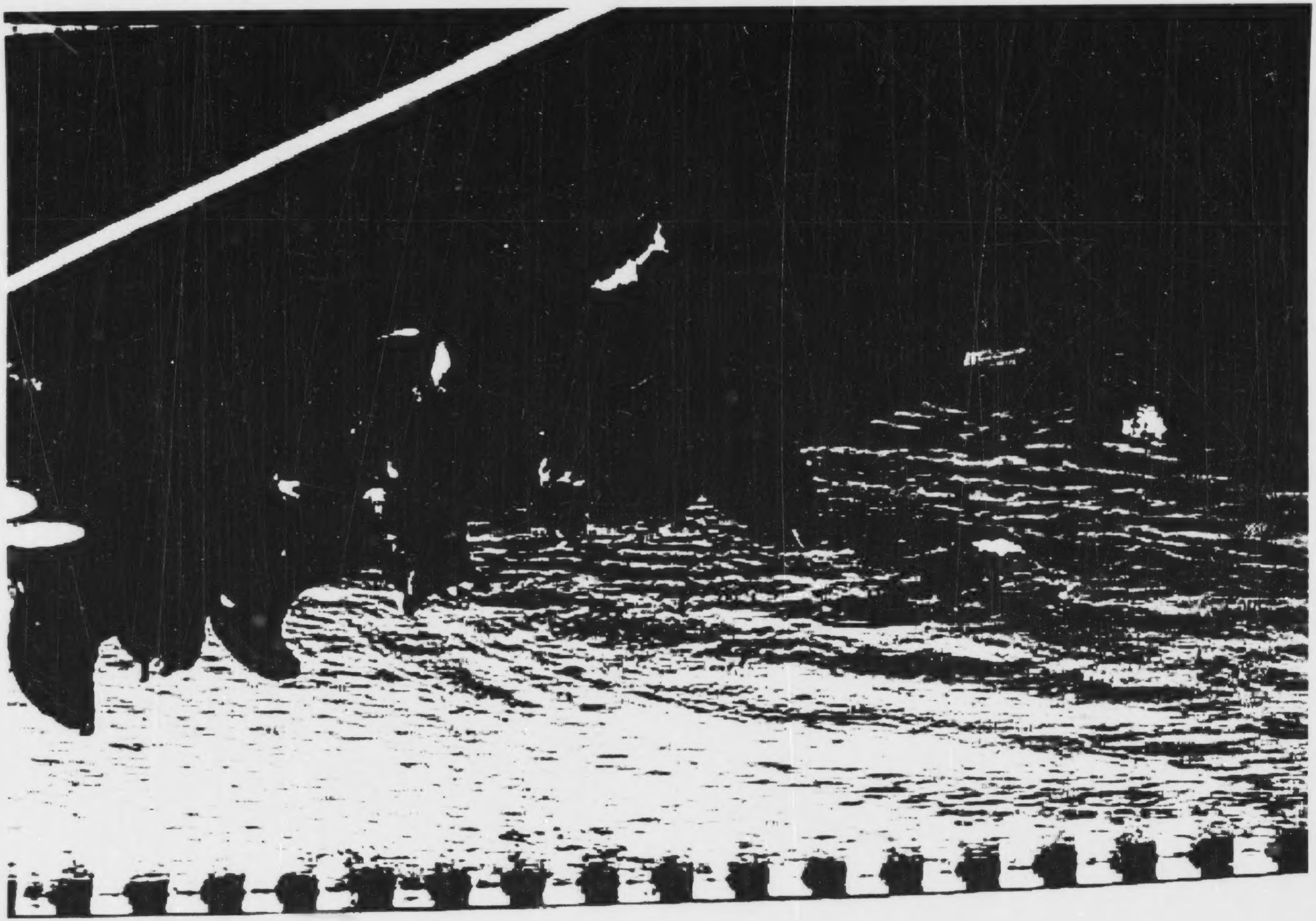
Categorisation of Substances found in Submarine Atmospheres

Any Questions?

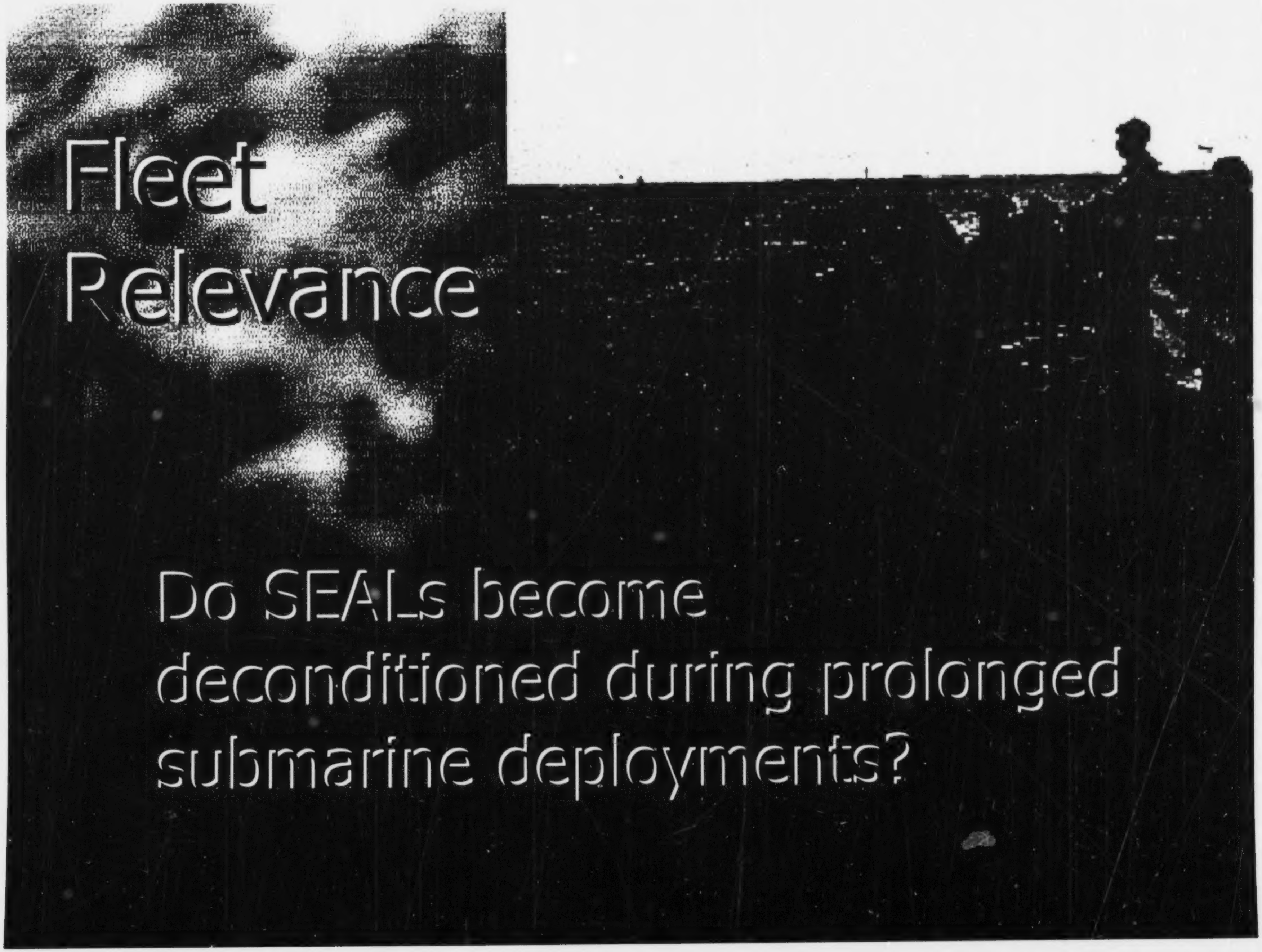


EFFECTS OF A PROLONGED SUBMARINE DEPLOYMENT ON SPECIAL OPERATIONS FORCES MISSION-RELATED PERFORMANCE

Dr. David Fothergill
LT John P. Sims, MC, UMO
Dr. Christine Schlichting
Naval Submarine Medical Research Lab
Department of Operational Medicine
Groton, CT 06349

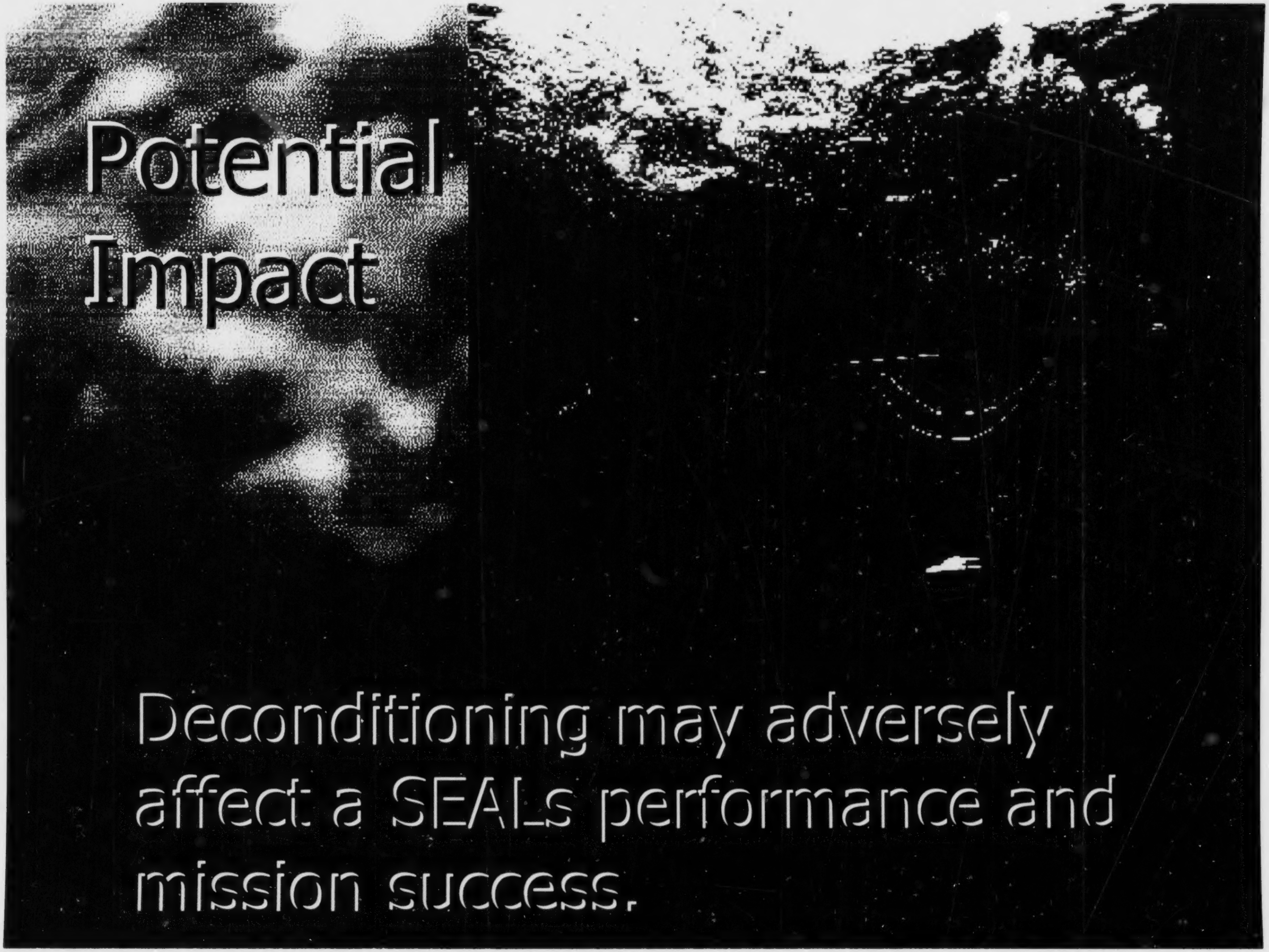


SEAL OPERATIONS



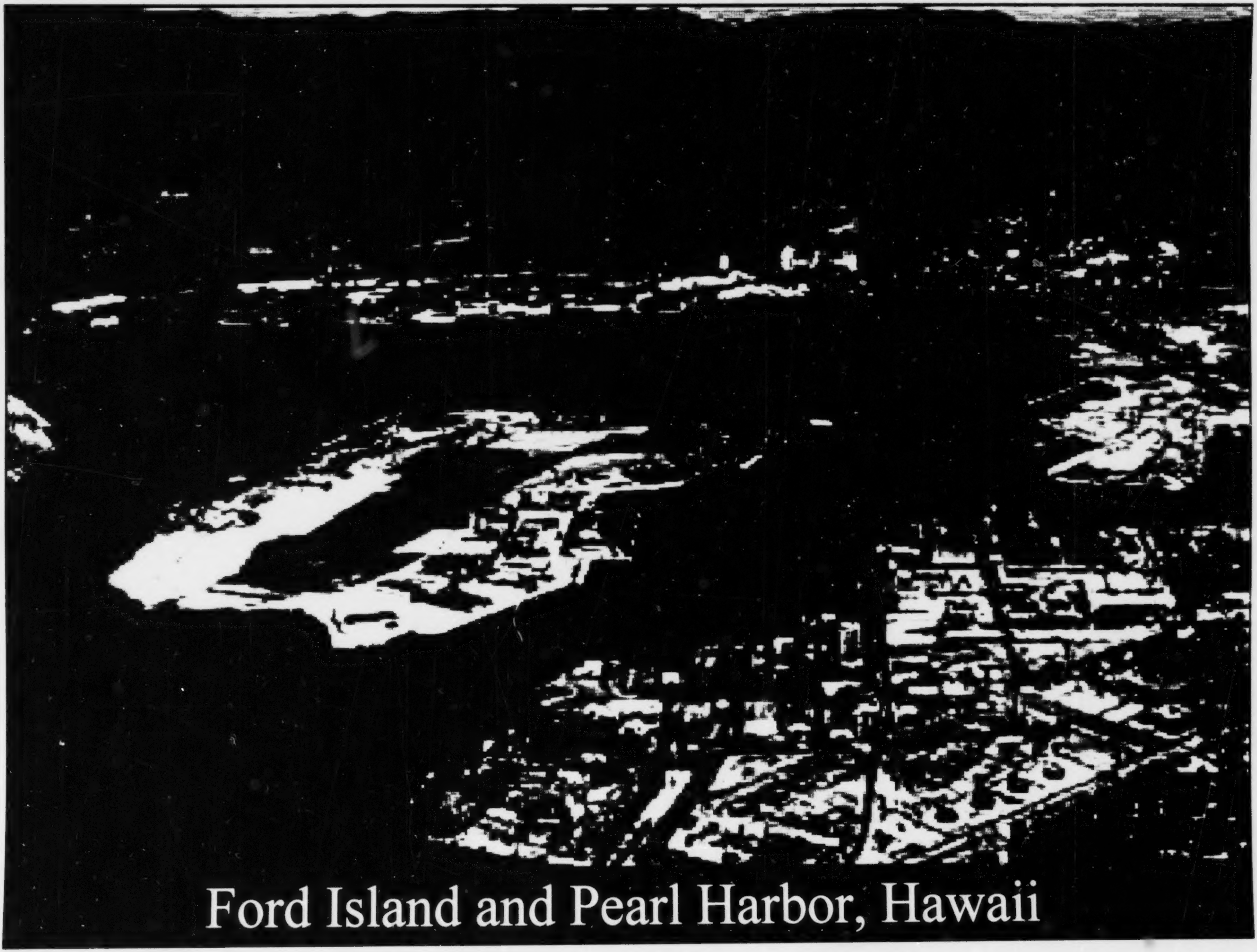
Fleet Relevance

Do SEALs become deconditioned during prolonged submarine deployments?



Potential Impact

Deconditioning may adversely affect a SEALs performance and mission success.



Ford Island and Pearl Harbor, Hawaii

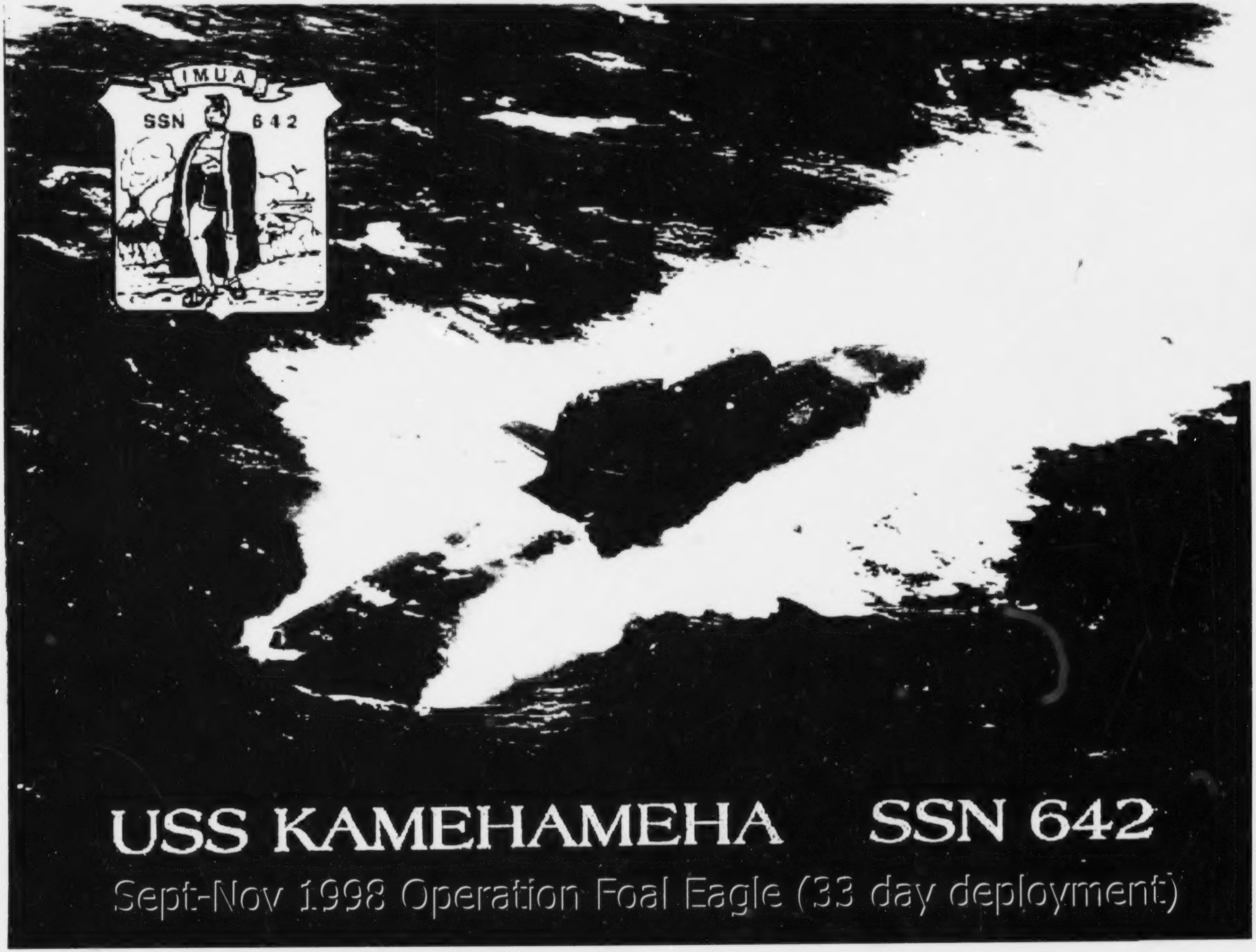
Approach

USS KAMEHAMEHA SSN 642

Field based study

Data collection

- one week pre deployment
- 33 day deployment (SEALs), 53 day deployment Submariners
- one week post deployment


IMUA
SSN 642

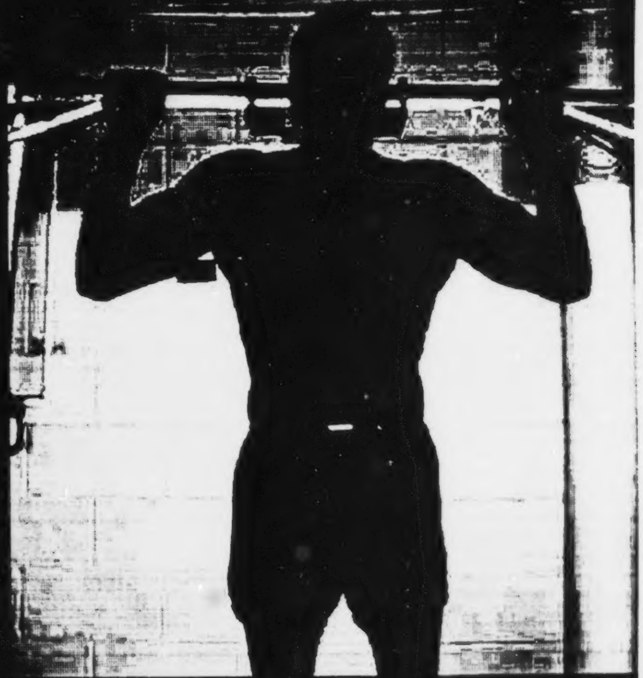
USS KAMEHAMEHA SSN 642

Sept-Nov 1998 Operation Foal Eagle (33 day deployment)

SUBJECTS

- U.S. Navy SEALs / SDV Team One
  - 10 deployed SEALs (DST)
    - mean age = 29.2 yrs,
  - 9 non deployed (controls) SEALs
    - mean ages = 29.7 yrs,
- 12 submariners (28 yrs)

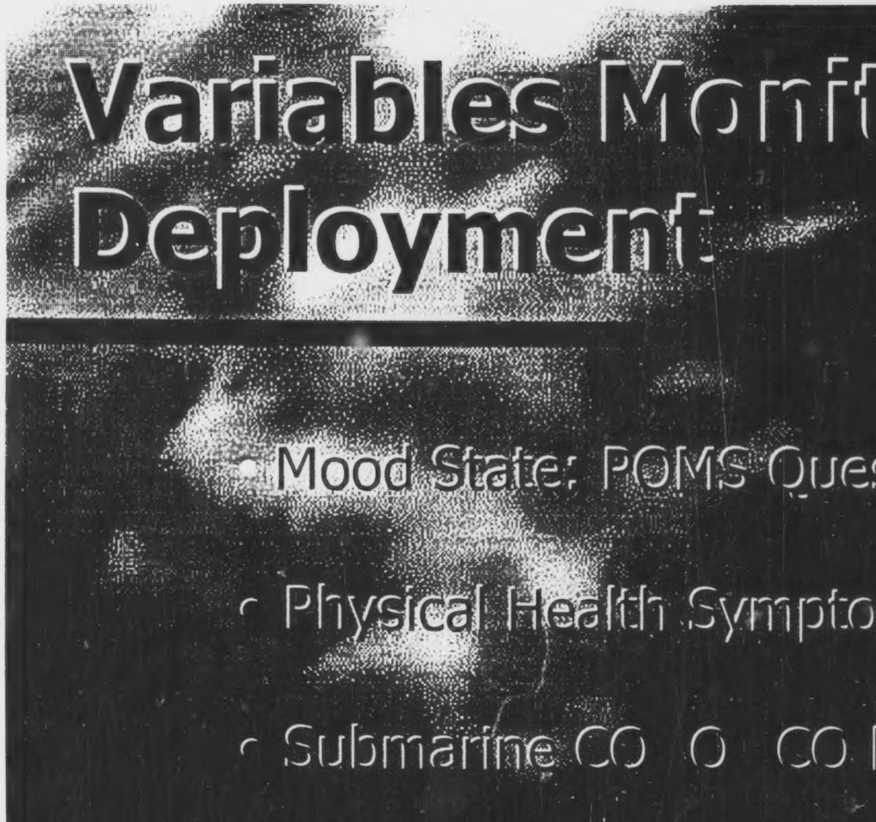
Pre-post Performance Measures



NMPI SOF Mission-Related Performance Battery

- Physical:
  - Shooting (laser adapted M16)
  - muscular strength, endurance (pull ups, grip strength)
  - Manual dexterity (M16 disassembly/assembly)
  - anaerobic performance (1-min step test with weight vest)
- Cognitive: NMPI computerized PAB

Aerobic Performance: 12 min run



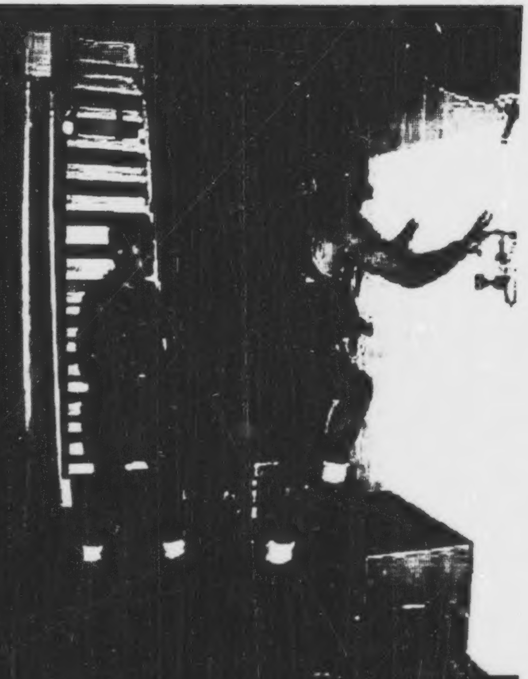
Variables Monitored During Deployment

- Mood State: POMS Questionnaire
- Physical Health Symptoms: WRAIR Questionnaire
- Submarine CO O CO levels (CAMS-I)
- Activity Levels: Self reported logs

Key Findings

- Control SEALS
  - No change in any performance variables during study.
- Deployed SEALS (deployment)
  - ⇑ annoyance, frustration, discouragement, depression, irritability, tiredness.
  - ⇓ contentment, energy, activity levels.
  - ⇑ freq. of sinus troubles, headaches, backaches, constipation, cuts/sores.
  - ⇓ freq. of muscle aches.

Key Findings cont.



- Deployed SEALS (post deployment)
  - ⇓ Aerobic performance

    7% ⇓ in distance run with no change in mean or max exercise HP.

    HP recovery 48% longer.
  - ⇓ Anaerobic performance

    9% ⇓ in # steps achieved in 1 min.

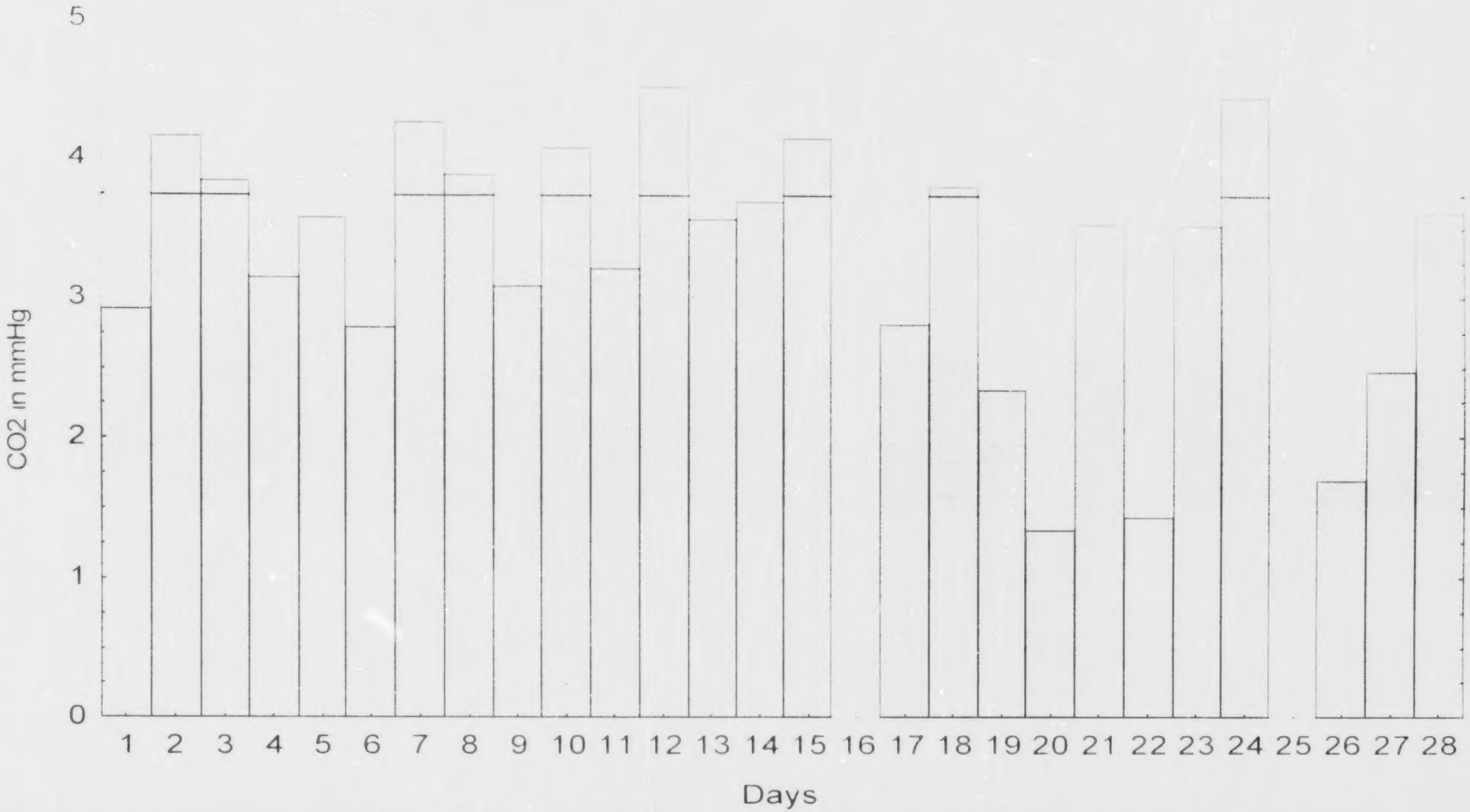
Key Findings cont.

Deployed SEALS

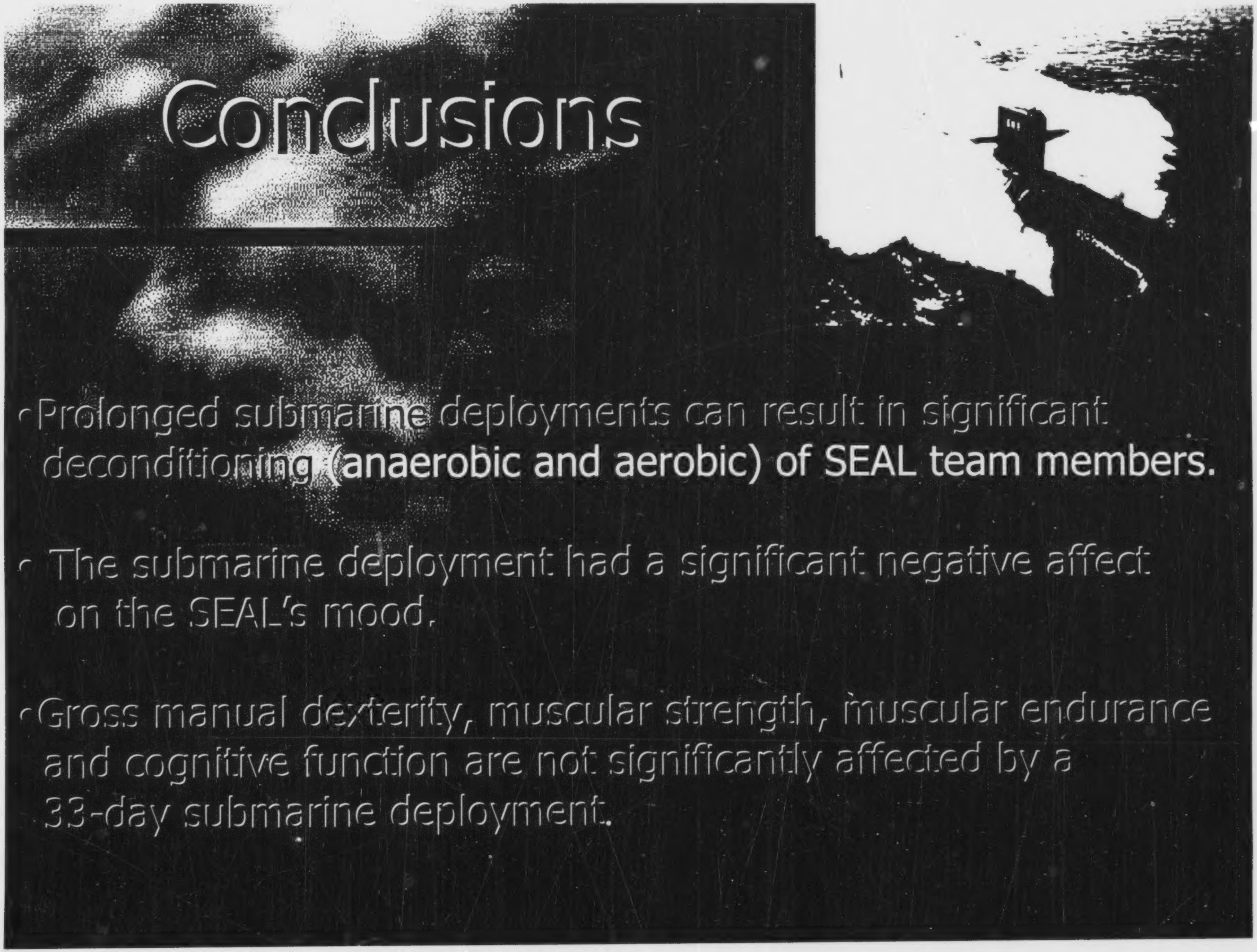
- No change in strength/dexterity/shooting
- No change in cognitive function
- Reduced time spent exercising during deployment relative to control SEALs (0.7 vs 2.5 hrs/day, $p<0.01$)

Submarine atmosphere Monitoring

Daily Mean Carbon Dioxide Levels in Fan Room



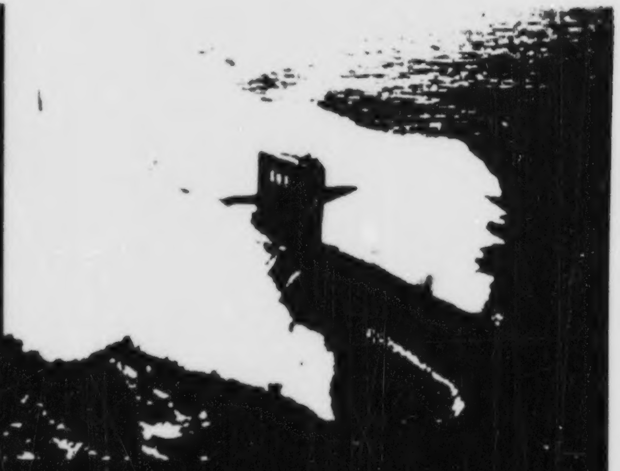
Daily mean CO2 levels exceeded the 3.8 mmHg limit for 9 of the 26 days



Conclusions

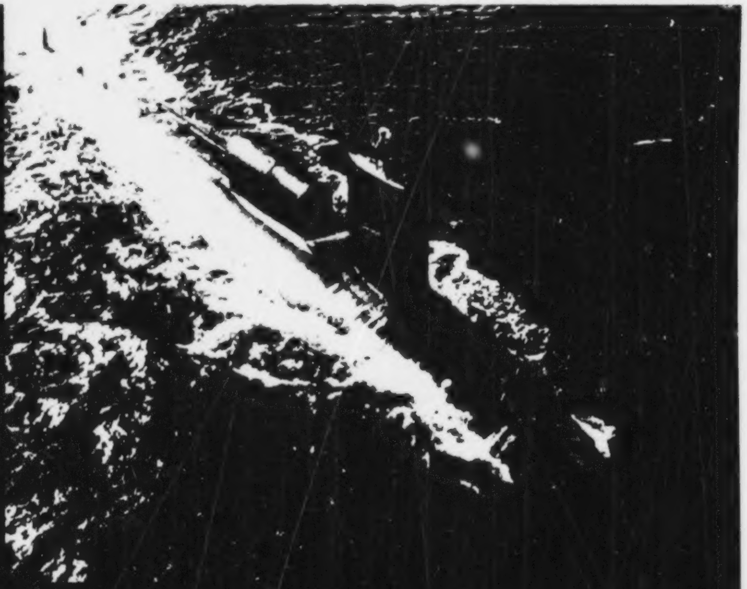
- Prolonged submarine deployments can result in significant deconditioning (anaerobic and aerobic) of SEAL team members.
- The submarine deployment had a significant negative affect on the SEAL's mood.
- Gross manual dexterity, muscular strength, muscular endurance and cognitive function are not significantly affected by a 33-day submarine deployment.

Conclusions



- Habitability issues that may impact SEAL mission performance include:
  - Reduced amount of physical activity (especially running).
  - Increased frequency of medical ailments:-
    - i.e. sinus problems and DDS ops.

Issues



- Converted ballistic missile subs slated to go away.
- DDS ops to be run from smaller fast attack submarines.
- Performance ⇓ of SEALs following prolonged deployment on fast attack subs are unknown.

Application of the Global Assessment System for Humans (GASH) to Evaluation of Submarine Atmosphere Exposure Effects

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Naval Health Research Center Detachment (Toxicology)
2612 Fifth Street, Bldg 433
Wright-Patterson Air Force Base, OH 45433
[2]Chief of Naval Operations
Human Systems Integration
FOB#2 Navy Annex Room 2625
Washington, DC 20370

The Global Assessment System for Humans (GASH)

- Battery of neurobehavioral tests designed to test integrity of different performance factors
  - detect subtle and clear changes in performance capacity due to known and unknown exposures
  - establish a database of signature response patterns for future risk assessment

Performance Factors

- *General Neurological Activity
  - excitatory processes and inhibitory tone
  - attention and vigilance
- *Cognitive Capacities
  - learning
  - memory
  - decision making
  - multi-tasking
- *Motor System Integrity
- *Sensory Processes
- Physiological Irritancy
- Emotionality
- Motivational Processes
- Social Behaviors

Sample GASH tests

- Electroencephalography (EEG)
  - general neurological activity
  - cognitive capacity

Real-time EEG Recording

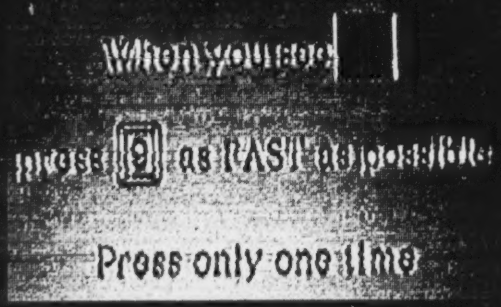
EPOCH: 1 / 52
GAIN:32K SR:128 STAT:INC HP:OFF
REL

Topographic Mapping
of Brain Responses

Sample GASH tests

- Behavioral Assessment and Research System (BARS)
  - general neurological activity
  - motor system integrity
  - sensory processes
  - motivational processes
  - cognitive capacity

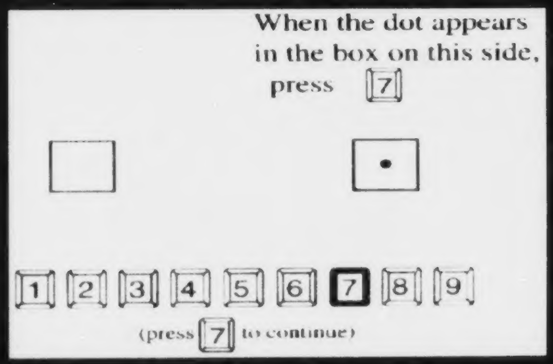
Sample BARS Tests



When you see

press 9 as FAST as possible

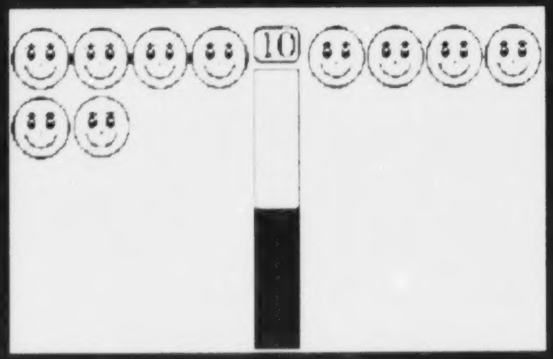
Press only one time

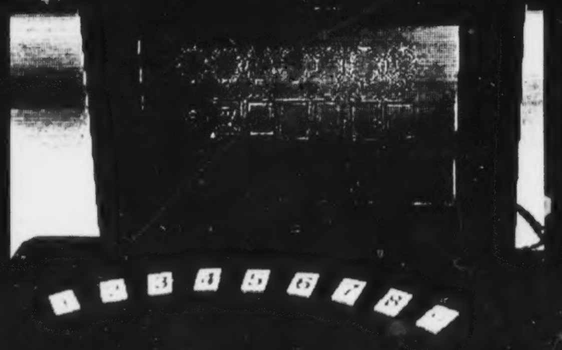


When the dot appears
in the box on this side,
press 7

1 2 3 4 5 6 7 8 9

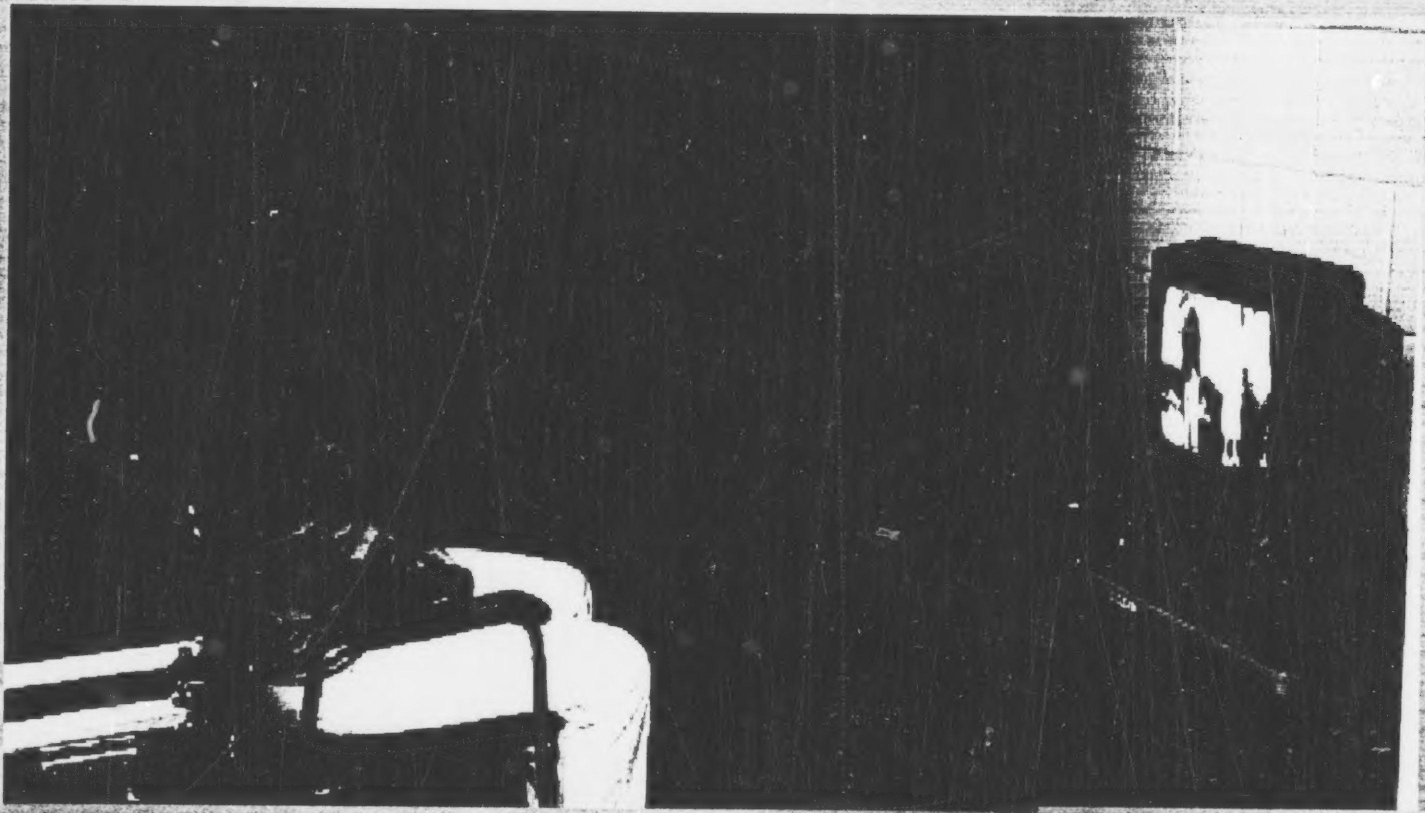
(press 7 to continue)

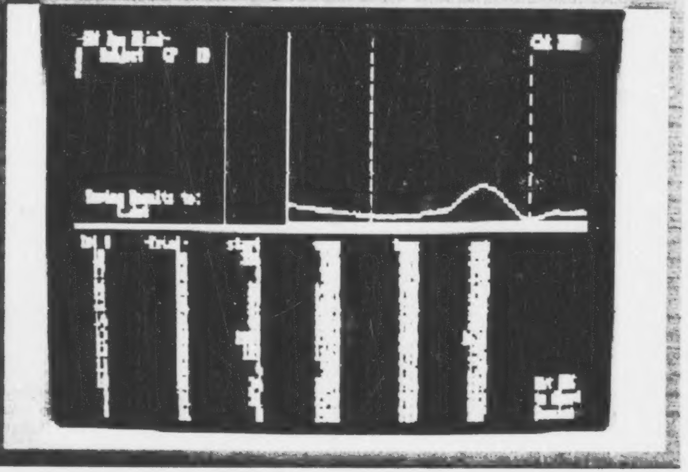




Sample GASH tests

- Acoustic Startle/Pre-pulse Inhibition
  - general neurological activity
- Eyeblink Conditioning Response
  - general neurological activity

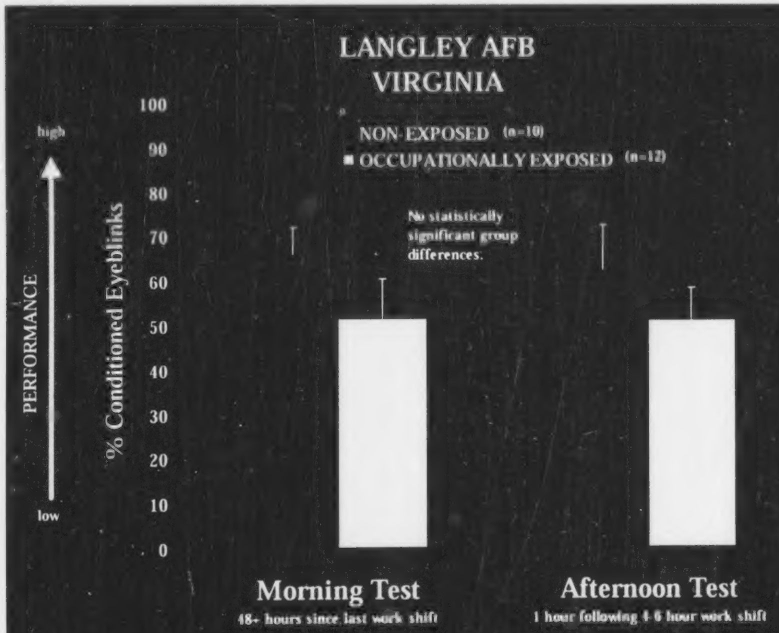


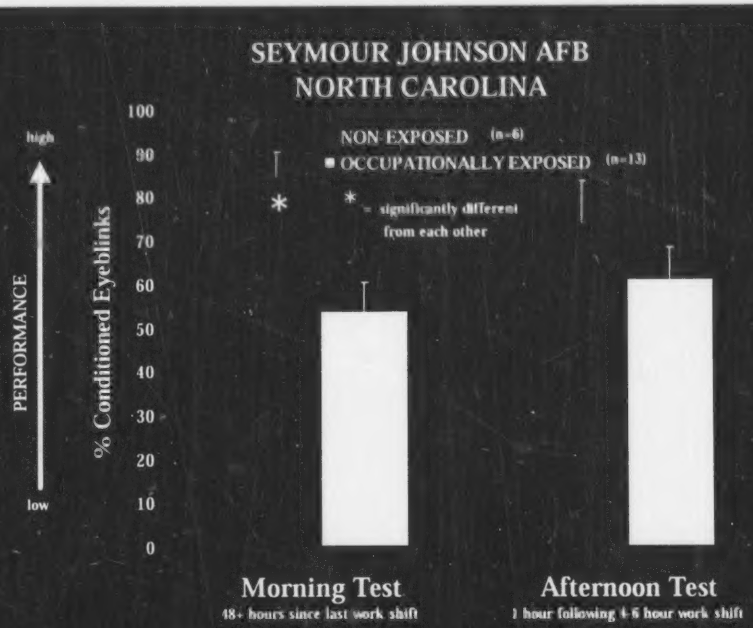


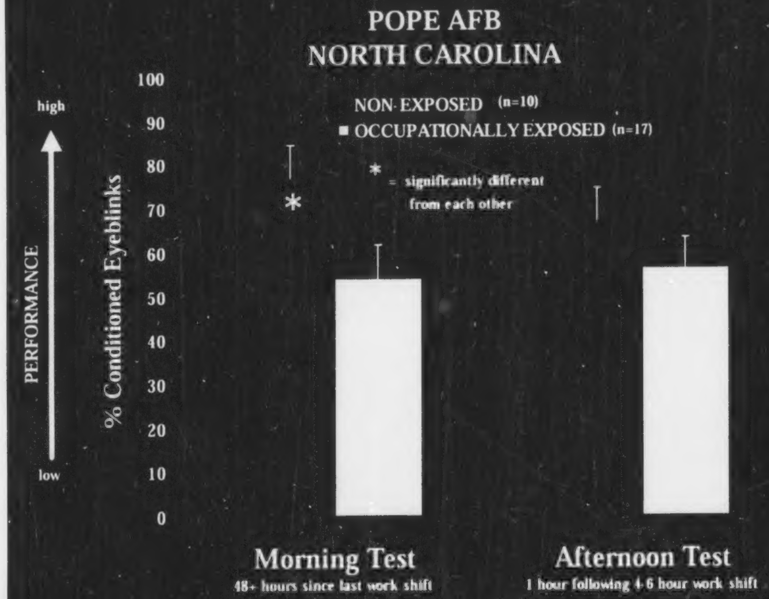
Eyeblink Conditioning Test Station and Sample Recording

Eyeblink Conditioning Response

- Testing effects of occupational JP-8 exposure in Air Force personnel
  - Experimental Group: personnel occupationally exposed during cleaning or repairing interior of aircraft fuel tanks
  - Control Group: other enlisted personnel with little to no occupational JP-8 exposure
- Methods
  - Test enlisted personnel at 6 different domestic bases
  - Test for acute and chronic effects
    - morning test at least 24 hours since last shift (chronic)
    - afternoon test immediately following 4-6 hours of occupational exposure (acute)
  - Assess various molecular, physiological, and neuropsychological endpoints
  - Use regression analysis of multiple endpoints for risk assessment


LANGLEY AFB
VIRGINIA


SEYMOUR JOHNSON AFB
NORTH CAROLINA


POPE AFB
NORTH CAROLINA

- Preliminary analyses provide evidence for chronic effect. Note the pattern in results from both morning and afternoon test sessions.

- Conclusion: Eyeblink conditioning is sufficiently sensitive to indicate exposure effects. This suggests it is appropriate to include in a risk assessment test battery.

End Product

- includes all appropriate neurobehavioral tests
- transportable to any field, laboratory, or hospital setting
- miniaturized hardware system that can be worn as a belt-pack
- real-time feedback to subject
- real-time feedback to others

Benefits of the GASH

- Monitor neurobehavioral integrity based on performance factors
- Assess effects of undetectable compounds or sub-threshold concentrations
- Eliminate need to systematically investigate all possible exposures and combinations/interactions
- Cross-validate with animal models
  - comparative analyses
- Identify signature response patterns to determine "% of maximal readiness"

GASH Applications

- assess possible effects of exposure to existing and new submarine materiel
- evaluate interactions between submarine atmospheres and stressors (psychological and physiological)
- evaluate effects of proposed performance enhancing chemicals or systems
- evaluate effectiveness of prophylactics or medical treatments for submarine-related illnesses
- evaluate continuing performance level before, during, and following underway assignment

Optimising the Air quality in Dutch Submarines

S. van der Gijp

J. Albers, H. van Es, P. Feron

Outline

TNO

Membrane gas absorption

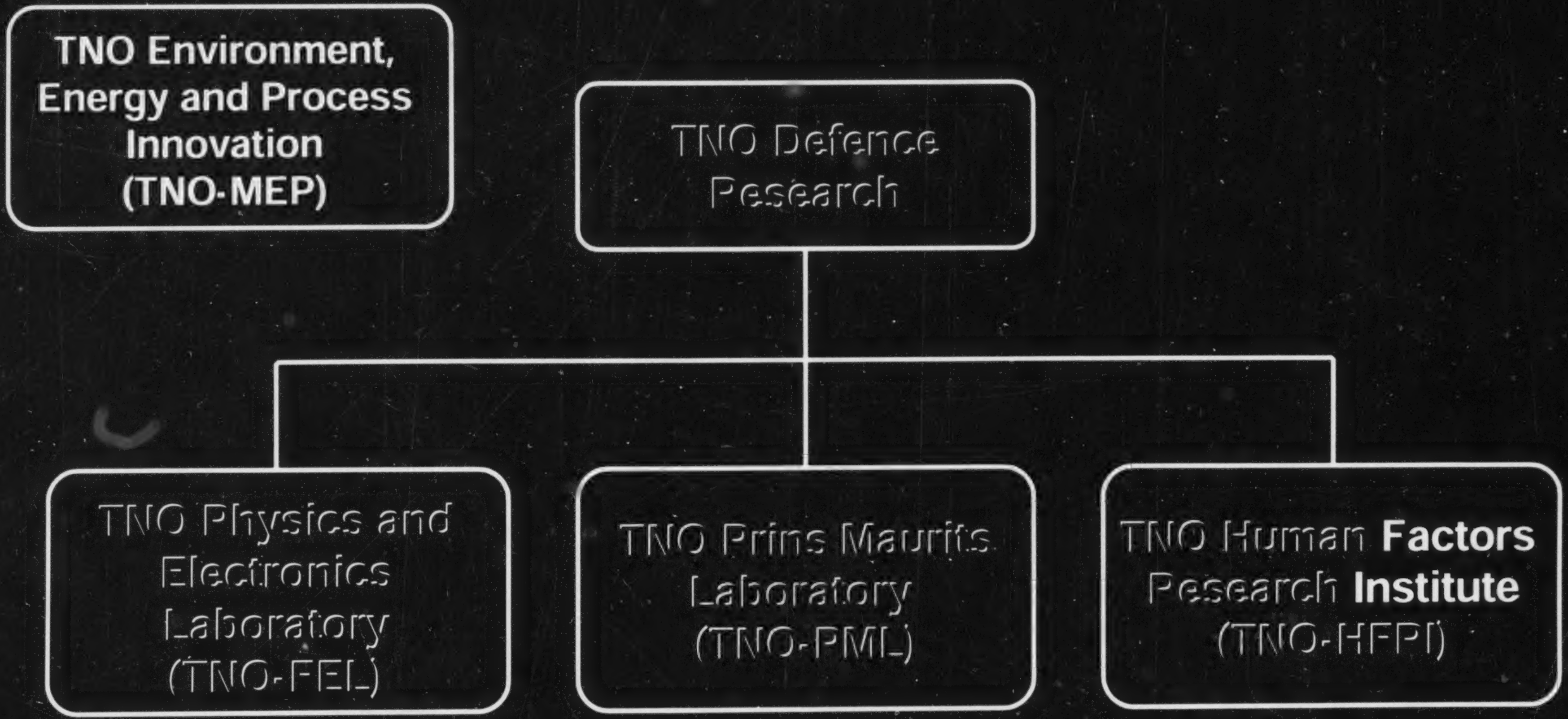
- working principle
- capabilities

Monitoring air quality

- hydrocarbons
- carbon dioxide

TNO Defence Research

Organisation



TNO Environment, Energy and Process Innovation (TNO-MEP)

TNO Defence Research

TNO Physics and Electronics Laboratory (TNO-FEL)

TNO Prins Maurits Laboratory (TNO-PML)

TNO Human **Factors** Research **Institute** (TNO-HFRI)

Research Areas TNO-DO

TNO-FEL

- Operational Research and Business Management
- Command & Control and Simulation
- Electronics & EOV
- Surveillance Systems
- Telecommunications and Defence Electronics

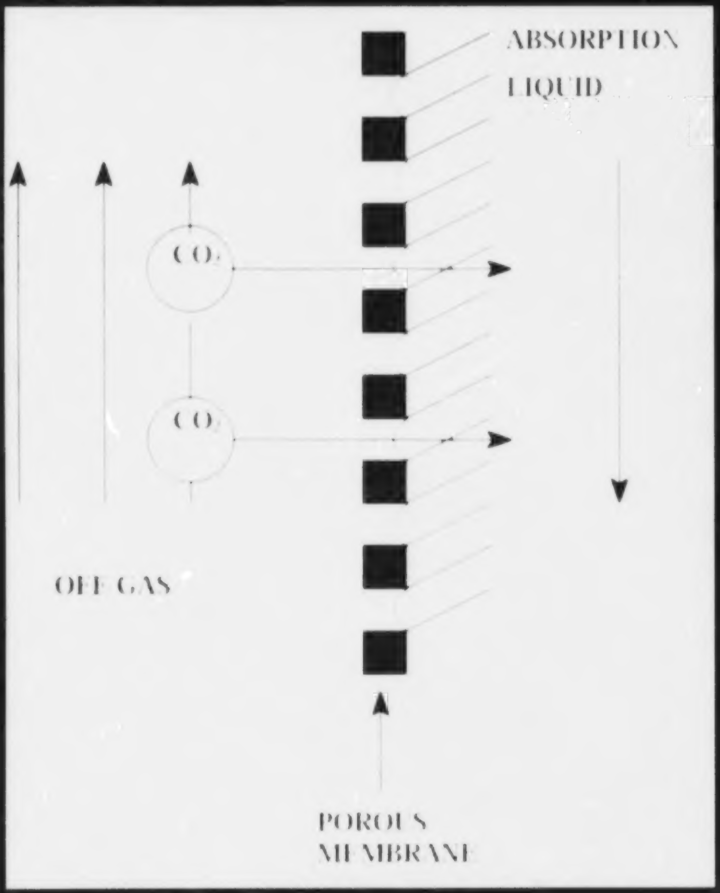
TNO-PML

- Toxic Substances
- Munition Technology and Explosion Safety
- Weapons and Weapon Platforms

TNO-HFRI

- Human Factors

Membrane Gas Absorption


ABSORPTION
LIQUID
CO₂
CO₂
OFF GAS
POROUS
MEMBRANE

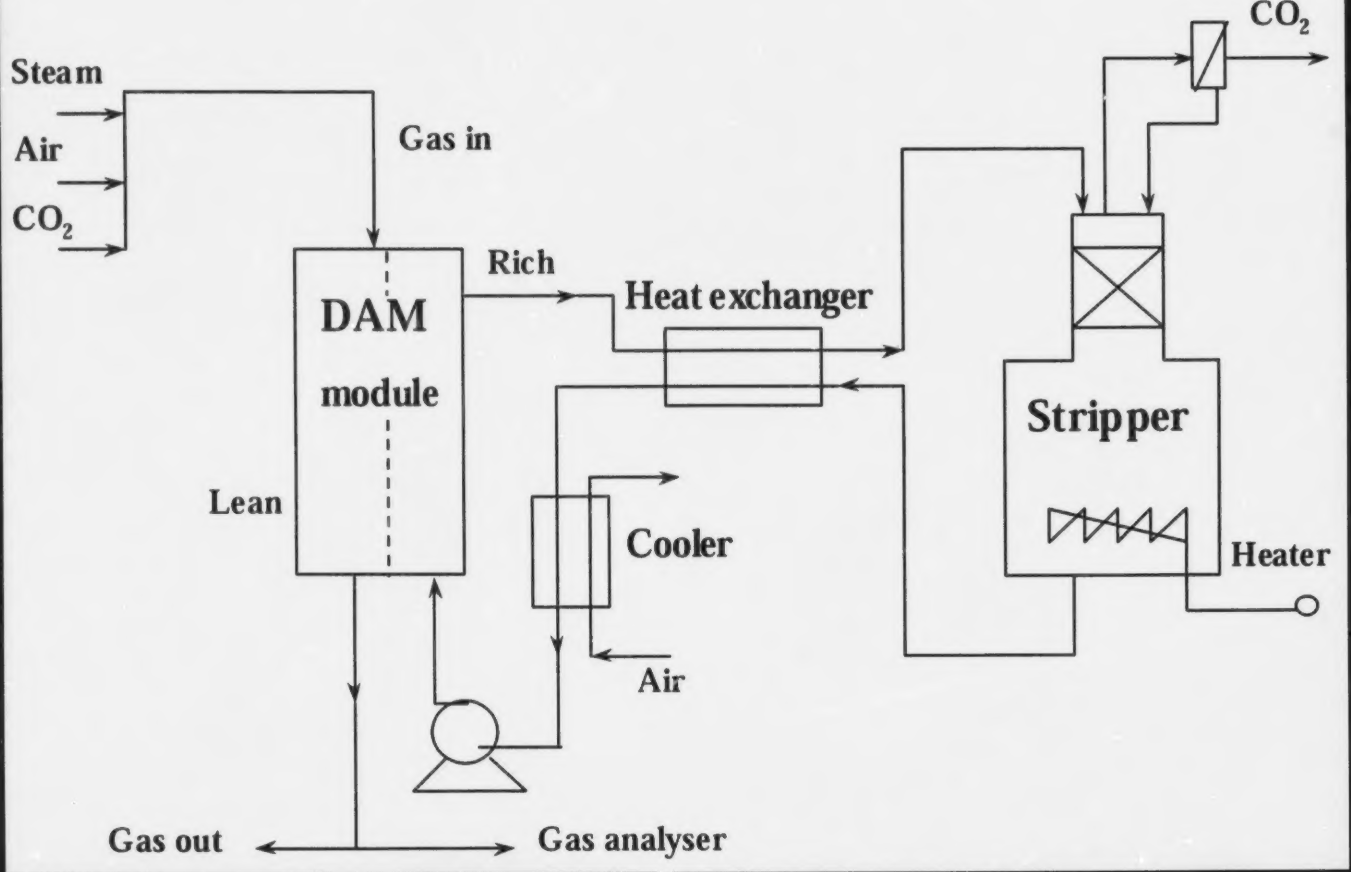
Capacity

- 0.5-1.5% reduced to 0.5%
- 2.5 kg CO_2/hour

CORAL

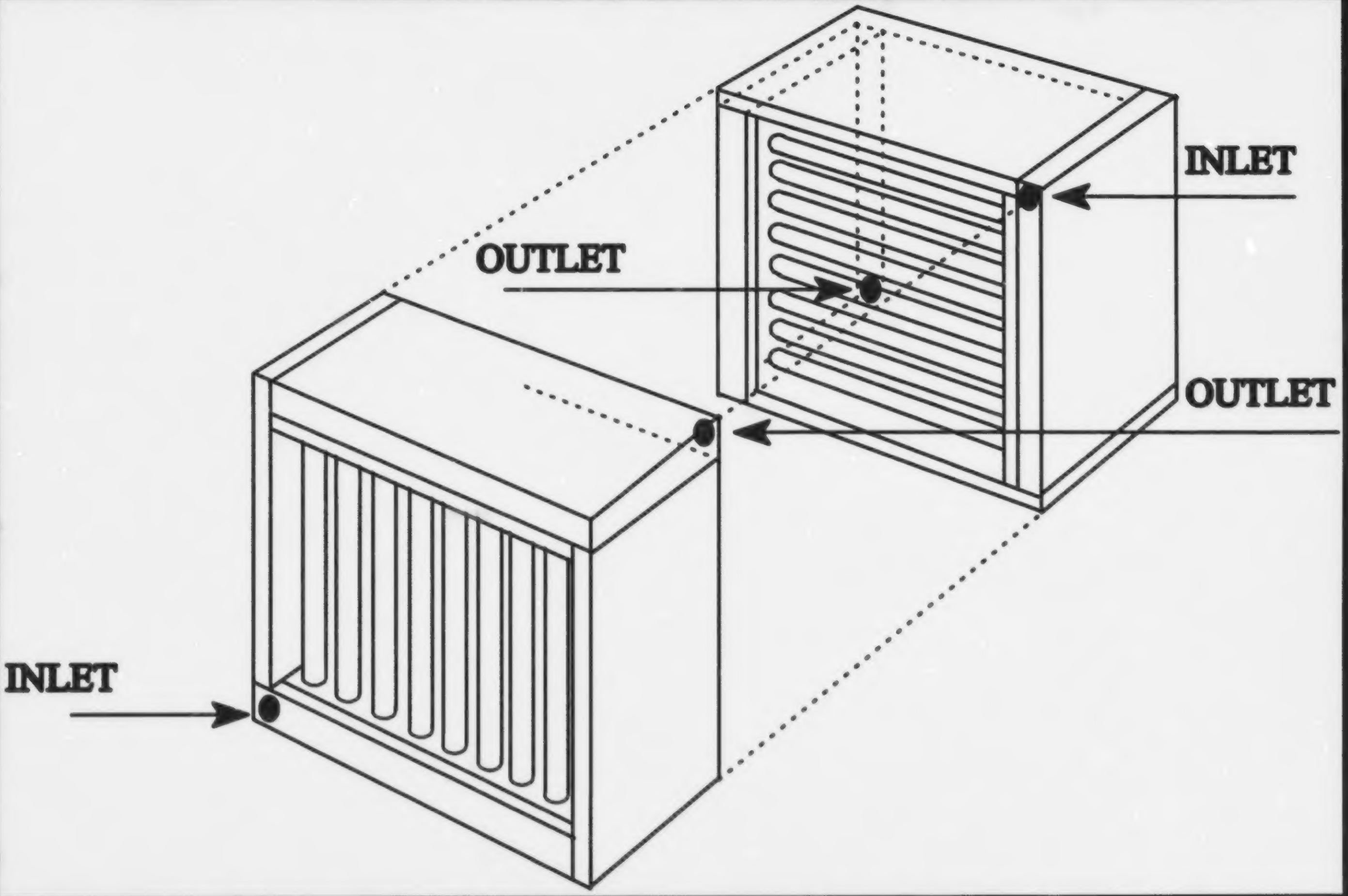
- less leakage
- no loss due to evaporation
- less corrosive
- withstands Oxygen

Schematic Overview



Steam
Air
CO_2
Gas in
DAM
module
Rich
Lean
Heat exchanger
Cooler
Air
Stripper
Heater
CO_2
Gas out
Gas analyser

DAM Module


INLET
OUTLET
OUTLET
INLET

Overboard

Injection

- easy
- noise

"Heineken" membranes

- pressure sensitive (yet)
- silent

Storage

(Dis)Advantages

4.1 kw/h

Continuous operation
- Less logistical burden

Less size

Less costs

Monitoring Air Quality

Charcoal filter replacement

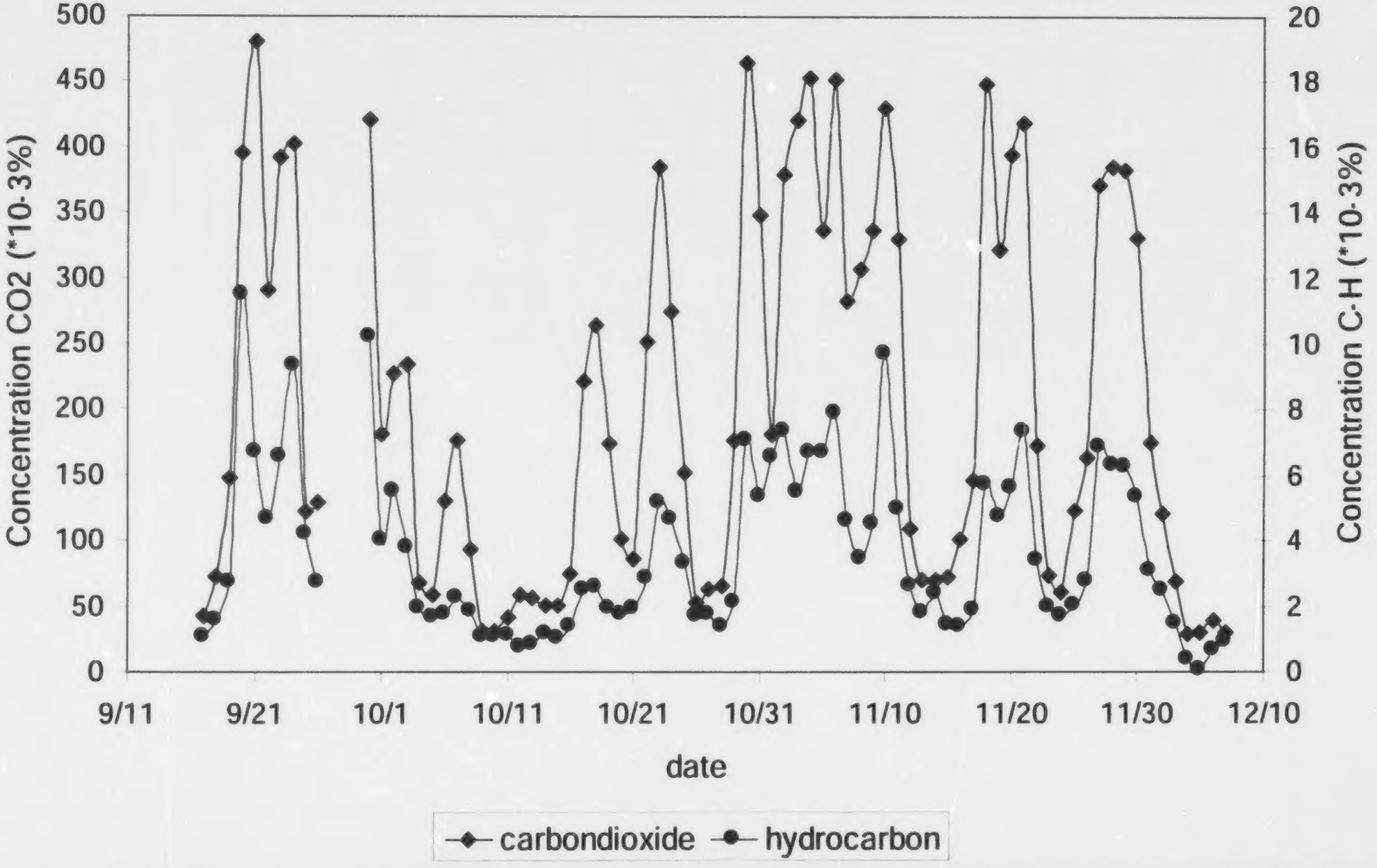
Membrane Gas absorption

AIP

Photo-Acoustic Sensor

- Hydrocarbon (C-H)
- Carbon dioxide (CO_2)

Results (I)

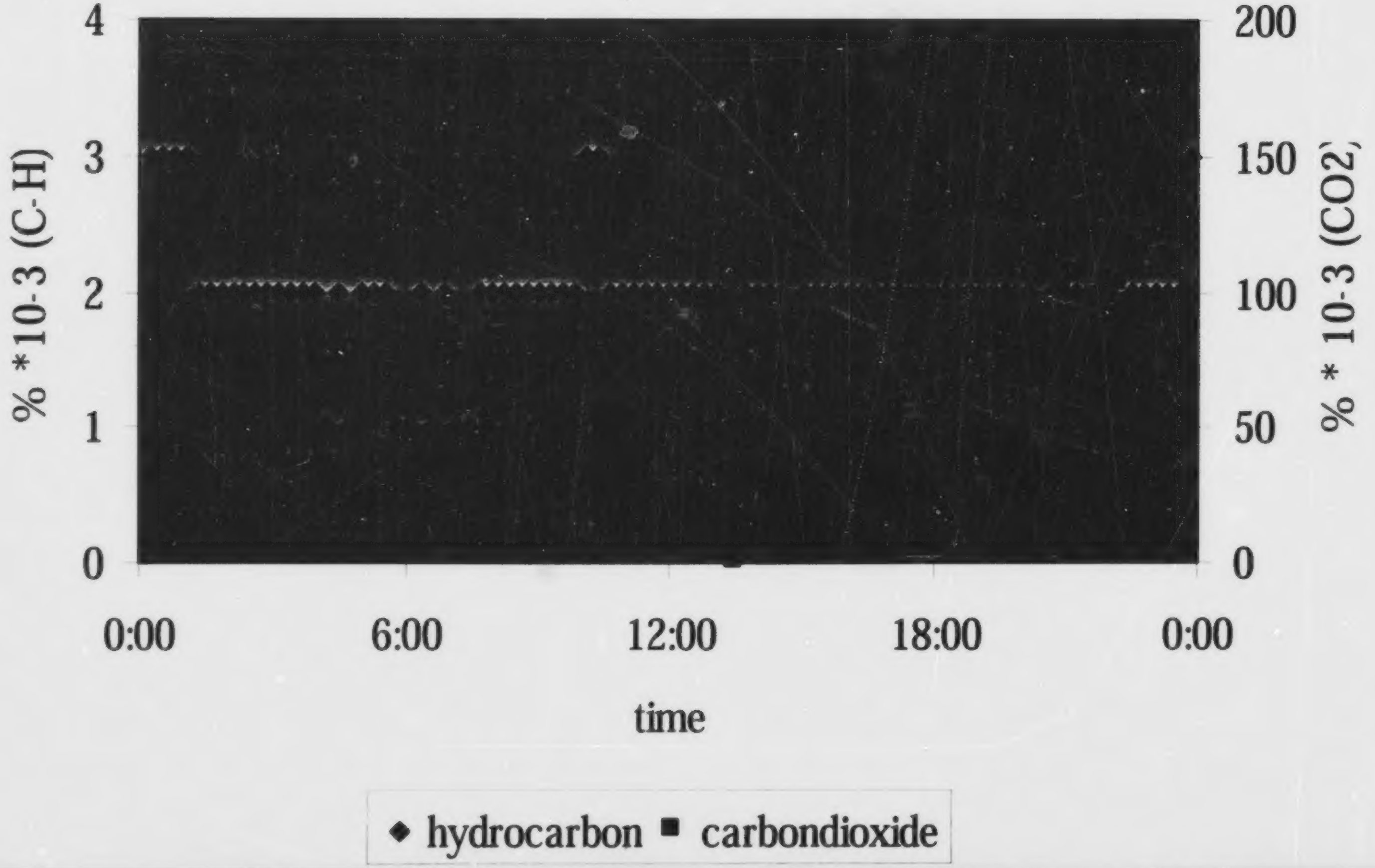

Concentration CO2 (*10-3%)
500
450
400
350
300
250
200
150
100
50
0
Concentration C-H (*10-3%)
20
18
16
14
12
10
8
6
4
2
0
9/11
9/21
10/1
10/11
10/21
10/31
11/10
11/20
11/30
12/10
date
carbondioxide
hydrocarbon

On Average

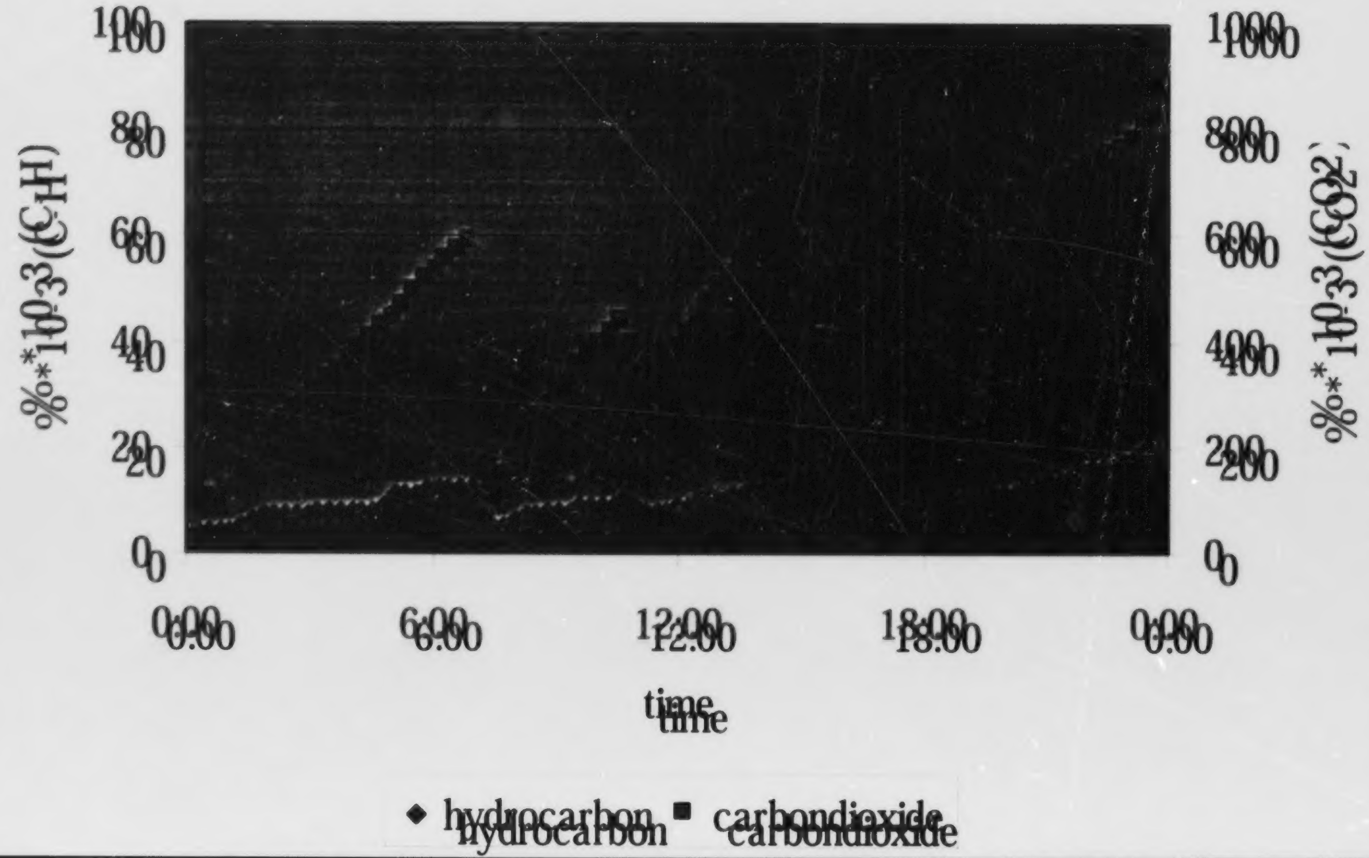
	Hydrocarbon (10^{-3}%)	CO_2 (10^{-3}%)
average	4	200
max.	65	870

- Well below SMAC levels

Results per day, low concentrations



Results per day, high concentration



Conclusions

Membrane Gas Absorption for the removal of CO_2 as developed by TNO has several advantages

- Less costs
- Less logistic burden
- Less volume

A prototype will be build this year

The monitoring study will be continued but shows no exposure to high concentrations hydrocarbons

Acknowledgements

DMKM
OZD
Hr. Ms. Zeeleeuw
TNO-MEP
Cirmac

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F +31 15 284 3963

gijp@pml.tno.nl
www.pml.tno.nl

SPACECRAFT MAXIMUM ALLOWABLE CONCENTRATIONS FOR AIRBORNE POLLUTANTS

John T. James, Ph.D.
NASA Johnson Space Center
Medical Sciences Division

SAMAP 2000

OVERVIEW OF PRESENTATION

Variability of Exposure Standards
Approach to Setting SMACs
Quality Factors for Standards
Uncertainty Factors
Relevancy of Animal Models
Scientific Approaches/Benchmark Dose
Time Extrapolations
Mixtures of pollutants
Conclusions

COMPARISON OF EXPOSURE STANDARDS (mg/m3)

Compound	TWA-TLV	180-d SMAC	360-d Russian PDK
Methanol	260	9	0.2
Ethanol	1900	2000	10
Isopropanol	960	150	1.5
Acetone	1200	50	2.0
Toluene	190	60	8.0
Xylenes	430	220	5.0
Ammonia	17	7	1.0
CO	30	10	5

CHANGES IN THE TLV FOR BENZENE

Year Set	TLV (ppm)
1946	100
1947	50
1957	25
1974	10
1990	0.1
1998	0.5

NATIONAL RESEARCH COUNCIL COMMITTEE ON TOXICOLOGY

- Groups of expert volunteers assembled into subcommittees for specific tasks
- Administrative coordination by NRC staff
- Has had a major role in setting U.S. military exposure standards
- Has had a major role in setting NASA astronaut exposure standards

SMACs

- Short-term values are set for contingency exposures of 1 and 24 hours- the risk of minor effects can be high, e.g. 1/10
- Long-term SMACs are set for nominal operations for continuous exposures of 7, 30, and 180 days- the risk of adverse effects is kept below 1/1000

QUALITY FACTORS FOR EXPOSURE STANDARDS

- Is the review group comprised of appropriate experts who are free of bias?
- Is the exposed population well defined?
- Are the acceptable risks clear to all?
- Is the documentation of values thorough and explicit?
- Are differences in key studies discussed?
- Is the rationale consistent across all compounds?

EXPERTS ON THE NRCCOT SMACs SUBCOMMITTEE

- Inhalation toxicologist
- Neurotoxicologist
- Toxicokineticist
- Reproductive & Developmental Toxicologist
- Genotoxicologist
- Epidemiologist
- Biostatistician
- Metabolism experts (2)
- Pathologist

TARGET POPULATION FOR SMACs

- Healthy adults from 35-60 years of age
- Space-flight effects are considered in setting SMACs for the following:
    - Hematotoxicants
    - Immunotoxicants
    - Cardiotoxicants
    - Radiomimetic compounds

"DEFAULT" UNCERTAINTY FACTORS

- Interspecies extrapolation- 10
- LOAEL to NOAEL- 10
- Intraspecies- 1
- Space- flight- 1, 3, or 5
- Small number of human subjects- 10/sqrt(n)
- Time extrapolation- Haber's Rule: CxT=k
- C is exposure concentration and T is exposure time
- Factors are combined in multiplicative way

RELEVANCE OF ANIMAL MODEL TO HUMAN SUSCEPTIBILITY

- Renal calcification in CO2 exposed Guinea Pigs is not representative of human response. We know this from submariner's exposures to CO2.
- Nephropathy in male rats exposed to hydrocarbons is due to high alpha-2-microglobulin, which is unique to male rats.
- Hormone-mediated thyroid injury in rodents is not representative of human exposure because of much higher levels of thyroid hormone in rodents than in humans.

SCIENTIFIC TOOLS

Pharmacokinetics can be used to predict target organ concentration, which can affect the interspecies extrapolation- e.g. modeling of exposure at 10 ppm furan showed 3- fold higher levels in the rat liver compared to "human" liver. Therefore, it would be wrong to assume that humans are 10- fold more susceptible than rats to liver toxicity.

Benchmark dose approach refines the LOAEL to NOAEL extrapolation by using the entire dose-response curve

BENCHMARK DOSE (BMD) APPROACH

- BMD is the maximum likelihood value for a given incidence of adverse effect, usually 10 % or 1 %.
- BMDL is the lower confidence value for a specified certainty from the BMD. We use a 95 % certainty. This value means that the BMD is not below the BMDL with a 95 % chance of being correct.
- A number of mathematical models can be used to represent the dose-response curve and predict the BMD and BMDL. These include probit, logistic and gamma multi-hit.
- The BMDs, and especially the BMDLs, can be very sensitive to the model chosen, even when the model provides a good fit to the data (high P value).

BMD EXAMPLE USING FURAN INDUCED BILIARY HYPERPLASIA

Dose (mg/kg)	0	4	8	15
Incidence	0/10	4/10	9/10	10/10

The LOAEL is 4 mg/kg, there is not a NOAEL

Model	P	BMD01	BMDL01
Log probit	0.98	1.63 mg/kg	0.38 mg/kg
Logistic	0.80	0.46 mg/kg	0.15 mg/kg
Gamma	0.99	1.16 mg/kg	0.03 mg/kg

INTRASPECIES FACTORS

- NASA does not use this factor unless there is evidence of a population of people more susceptible than the typical population.
- Many agencies use an intraspecies factor because of the diversity of the population being exposed (e.g. the young, old, ill, etc).
- The SMAC for formaldehyde was set lower to protect a subpopulation of persons who seem extremely sensitive to its irritant properties.
- The ethanol SMAC was set in part by addressing persons who exhibit the “flushing” response to alcohol ingestion. This response is due to genetic differences in metabolism of acetaldehyde, which can accumulate in susceptible persons.

EXPOSURE TIME EXTRAPOLATIONS

- Haber's Rule (k=c x t) is the default approach. If the time of exposure increases 10-fold, then the safe exposure concentration should decrease by 10-fold. This is a very conservative approach.
- The ten Berge approach refines this by using exponents other than 1 for "c" and "t."
- $K = c^a \times t^b$
- It is rare that sufficient data are available to determine either of the exponents

ASSESSMENT OF EXPOSURE TO MIXTURES

- Our assumption is that compounds targeting the same organ or organ system can act additively in proportion to the individual exposure limits. For each toxicological group a toxicity index is calculated as follows:
- $T\ (grp) = C1/SMAC1 + C2/SMAC2\ldots Cn/SMACn$
- If T (grp) is less than 1 for each group, the the air is considered acceptable.
- Typical groups include:
  - Respiratory irritants
  - Nervous system depressants
  - Hematotoxicants
  - Cardiotoxicants
  - Carcinogens

CONCLUSIONS

- A high-quality process is used to set SMACs
- SMACs may not be applicable to populations other than astronauts.
- Attempts are being made to replace default approaches with scientific methods, but there is often insufficient data to enable the scientific process.
- Toxicology itself is not a complete science: By setting an exposure level, we hypothesize that the exposure limit is protective to a certain level of risk, but we never get a chance to test the hypothesis.

EnviroBio

DEVELOPMENT OF A BIOLOGICAL REACTOR FOR THE REMOVAL OF CARBON DIOXIDE FROM SUBMARINES

Systèmes EnviroBio Inc.
Québec, Canada

Nathalie Bernier, Sylvie Fradette, Michelle Plante, and Ken Johnson

EnviroBio

DEVELOPMENT OF A BIOLOGICAL REACTOR FOR THE REMOVAL OF CARBON DIOXIDE FROM SUBMARINES

- Work conducted under the Defence Industrial Research (DIR) Program
- EnviroBio Inc. started in 1997
- Development of platform(s) for reduction/recycling of CO_2

WHY?

- Common technology for CO_2 removal uses 2-aminoethanol (MEA) which:
  - is efficient but
  - expensive
  - requires significant energy for regeneration
  - is corrosive, toxic and volatile
  - forms ammonia upon decomposition ☞ another toxic material
- The solution: **immobilized carbonic anhydrase**

EnviroBio

- Carbonic anhydrase (CA) catalyzes following reaction:

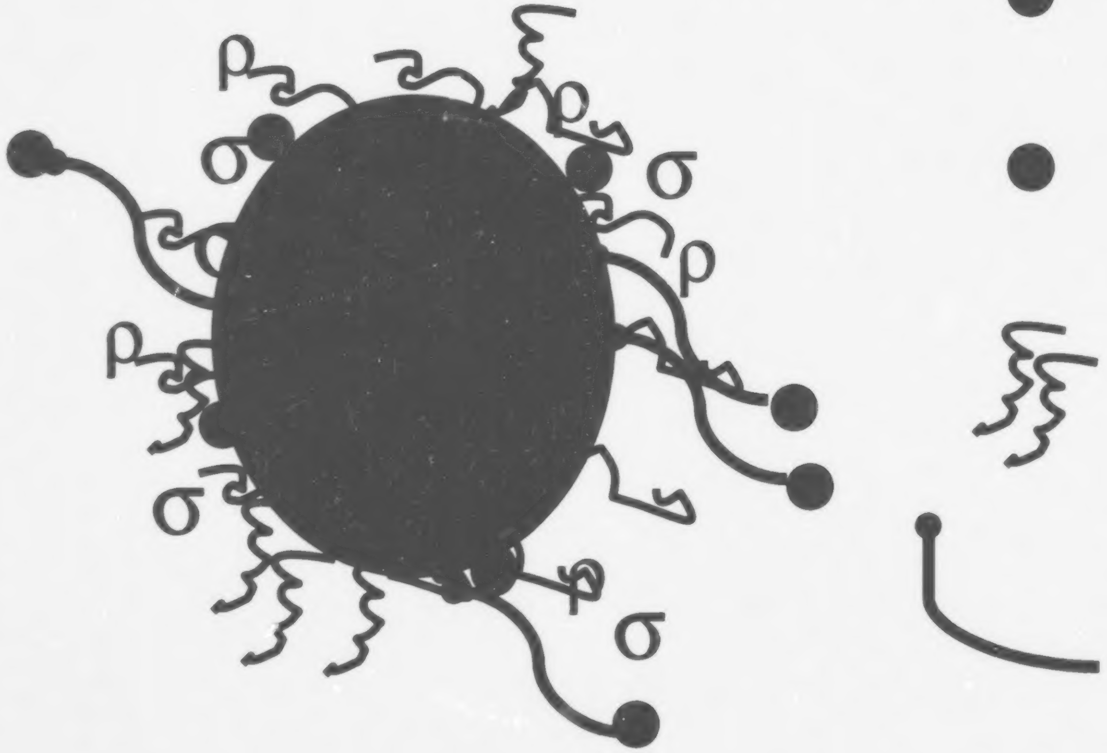
$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

- Molecular mass 30,000 kD
- Highest molecular turnover number of any known enzyme - 6 x 10^7 molecules of CO_2 hydrated per minute
- Ubiquitously distributed in nature
- Free enzyme highly stable
- Ideal molecular size for immobilization

IMMOBILIZATION/BIOREACTOR DESIGN STRATEGY

- Determination of best way to achieve greatest surface density of immobilized carbonic anhydrase per unit of solid surface
- Determination of how to achieve maximum activity per unit of solid surface
- Determination of optimal bioreactor design to optimize CO_2 hydration by CA
- Initial work conducted with PMMA microbeads ☞ scale-up

IMMOBILIZATION MATRIX



- ● CA without spacers
- ● CA with spacers
- Exterior ionic environment of matrix
- Chemical spacer

IMMOBILIZATION/BIOREACTOR DESIGN STUDIES

- variety of supports tested
- variety of immobilization methods tested
- variation of microenvironment of immobilized CA by use of acidic or alkaline supports
- immobilization with and without chemical spacers
- Polymethylmetacrylate (PMMA) determined to be best solid support

CHARACTERISTICS OF IMMOBILIZED CA ON PMMA

Immobilization Method	Enzyme Surface Density (molecules/ mm^2)	Activity (units/ mm^2)
Acidic	8.0×10^{10}	0.2
Alkaline	1.3×10^{9}	1.7

RATE OF REACTION

Enzyme Form	Reaction Rate (mol/L/s)
Free	3×10^{-5}
Immobilized	1.8×10^{-4}

EnviroBio

ENZYME STABILITY STUDIES

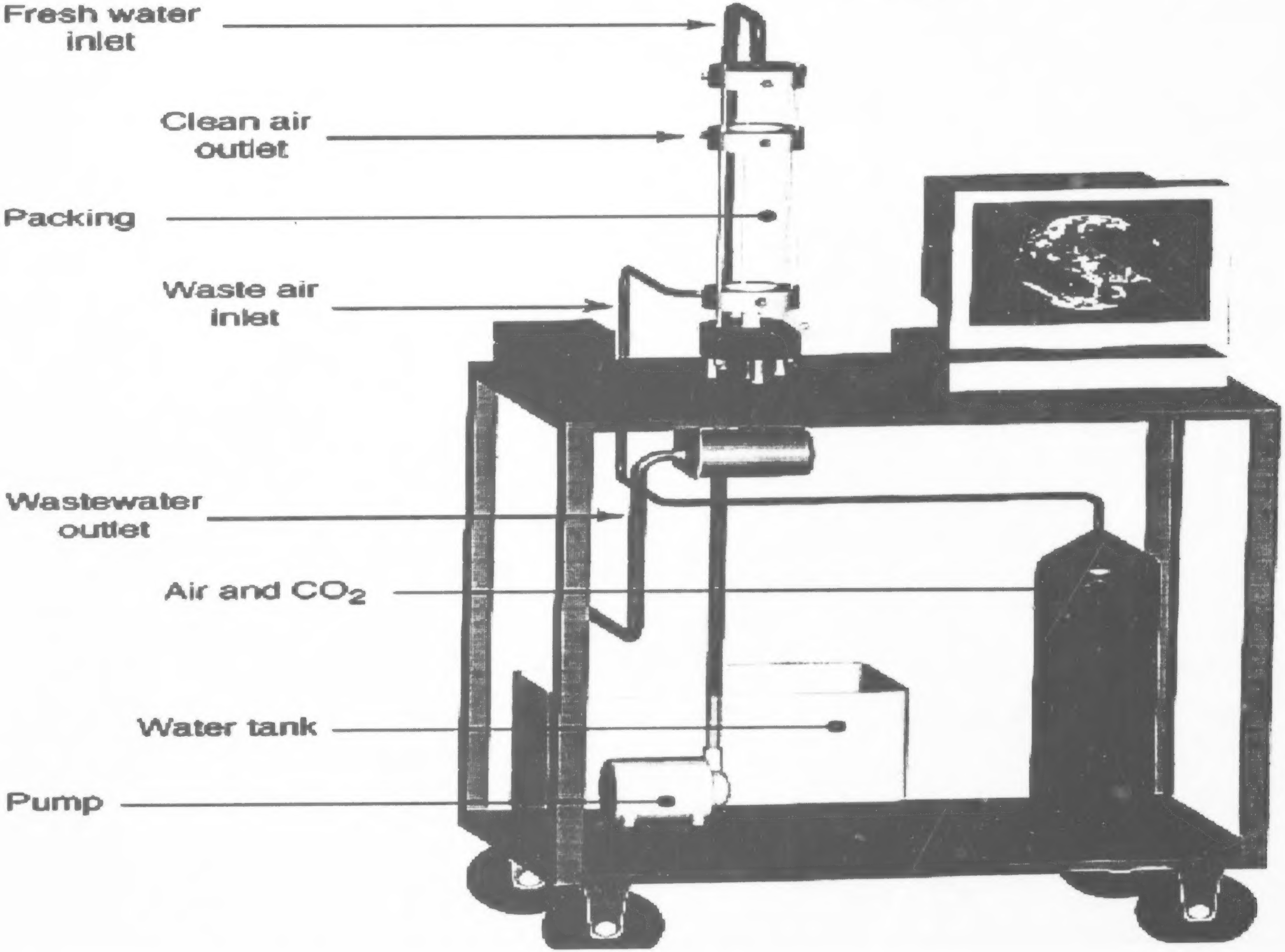
ENZYME FORM	TEMPERATURE (°C)	RELATIVE ACTIVITY (%) (6 weeks)
FREE CA	4	100
	22	100
	28	100
	37	100
IMMOBILIZED CA	4	100
	22	100
	28	100
	37	40

BIOREACTOR DESIGN CRITERIA

PARAMETER	VALUE
CREW SIZE	60 Persons
MISSION LENGTH	50 Days
MAINTAINED CO_2 LEVEL	0.5% (v/v)
AVAILABLE SPACE	1.5 m^3

Bioreactor

EnviroBio..


Fresh water inlet
Clean air outlet
Packing
Waste air inlet
Wastewater outlet
Air and CO_2
Water tank
Pump

CONCLUSIONS

- feasible to immobilize carbonic anhydrase
- immobilization protocols involving use of chemical spacers preferable
- alkaline immobilization surfaces bind less CA but the enzyme activity is much greater under alkaline conditions
- immobilized CA converts CO_2 six times more rapidly than free CA
- immobilized CA is stable, especially at lower temperatures

WAY AHEAD

- kinetic analysis of immobilized CA in experimental bioreactor under conditions close to those found in submarines
- optimization of bioreactor design with respect to dimensions, flow rates, etc
- construction of prototype for testing efficiency of CO_2 removal in submarines

DEVELOPMENT AND USE OF REAL-TIME DETECTORS ABOARD U.S. SPACECRAFT

T. Limero, S. Beck, E. Reese, and J. Trowbridge
(Wyle Laboratories)

John T. James (NASA/Johnson Space Center)

Presentation Outline

- Early History of Real-Time Monitors
- Air Quality Degradations in Spacecraft
- Need for Real-Time Monitors
- Compound Specific Analyzers
- Multiple Compound Analyzer-VOA
- Future Work
- Conclusions

Real-Time Monitoring on U.S. Spacecraft Prior to 1990

- Most assessments of air quality were by archival methods
- Only major constituents have been routinely monitored
  - Oxygen, Carbon Dioxide
  - Water Vapor as dew point
  - Pressure and Temperature
- Drager tubes used on Skylab because of heat shield failure

Skylab Operations

Drager Tubes
used to evaluate TDI
in the module before
crew entered because
the module was
overheated

Reasons For Development of Few Spacecraft Real - Time Monitors

- ◆ Short missions (5-14 days)
- ◆ Sensor technology limitations
- ◆ Resource constraints
  - size
  - power
  - microgravity compatibility
  - crew time
- ◆ Generally good air quality on spacecraft due to careful materials control

Series of Shuttle Thermodegradation Incidents

- STS-6 (1983)Overheated Wiring
  - Kapton-Teflon wired produced odor detected by crew
- STS-28 (1989) Teleprinter cable pyrolyzed
  - Kapton-Teflon wiring
- STS-35 (1990) Digital Display unit
  - Pungent odor released as component overheated due to clogged air filters

Need for Real-time Air Quality Monitors

- ◆ Provide data in contingency situations to crew and ground personnel
  - Extent of problem
  - Effectiveness of decontamination efforts
  - Conserve finite emergency resources, i.e., air
- ◆ Psychological benefits that real-time analysis provides the crew
  - Nominal conditions- air quality is acceptable
  - Following a contingency- air has been properly scrubbed

Development of Combustion Products Analyzer (CPA)

- Response to STS-28 thermodegradation
- Based on materials likely to be involved in a combustion event, sensors for four marker compounds were selected
  - Carbon monoxide, hydrogen cyanide, hydrogen chloride, and hydrogen fluoride
- Prototype CPA was readied and flown in Fall 1990
- CPA manifested on each Shuttle mission until replaced by CSA-CP this past year

CPA On Orbit

First Significant Use of CPA on Mir Station

- CPA manifested on Mir after SFOG event
- CPA detected high concentration of CO (>400 ppm) following BMP event
- Readings regarded as suspect because of no reported crew symptoms and known hydrogen cross-sensitivity of the CO sensor
- Archival samples confirmed CPA readings, post mission

Which is the Dangerous Situation?

SFOG Incident

Press Conference Similar
to this following BMP

Experience Shaped Monitoring Strategy for ISS

- Archival data collected on Shuttle and Mir was vital in identifying trace contaminants to be monitored for protection of crew health
- NASA/Mir program was NASA's transition to longer duration missions
- Better understanding of contingency events
  - Spills/Leaks such as ethylene glycol
  - Fires such as SFOG and BMP

Strategy Developed For ISS

- Compound Specific Analyzers
  - Portable, small monitors to detect a few reactive compounds (similar to CPA concept)
    - CSA-CP (Combustion products)
    - CSA-HZ (Hydrazines detector)
    - Carbon dioxide monitor (CDM)
- Volatile Organic Analyzer
  - Instrument that can detect and quantify 20 or more trace organic compounds and identify unknowns in spacecraft air
  - Current technology is fixed position

Improved CPA Developed for ISS: CSA-CP

- ◆ Smaller than CPA and can operate without a pump for long periods. Auxiliary pump is available
- ◆ Electrochemical Sensors
- ◆ CO sensor does not have the cross-sensitivity to hydrogen
- ◆ HF sensor is replaced with oxygen
  - A reliable HF sensor could not be found
  - Oxygen sensor serves as backup to ISS primary sensor

CSA-CP On Orbit and Operating Ranges

Compd	Conc. Range
	ppm
CO	3-1000
HCl	.1-100
HCN	.5-100
Oxygen	15%-30%

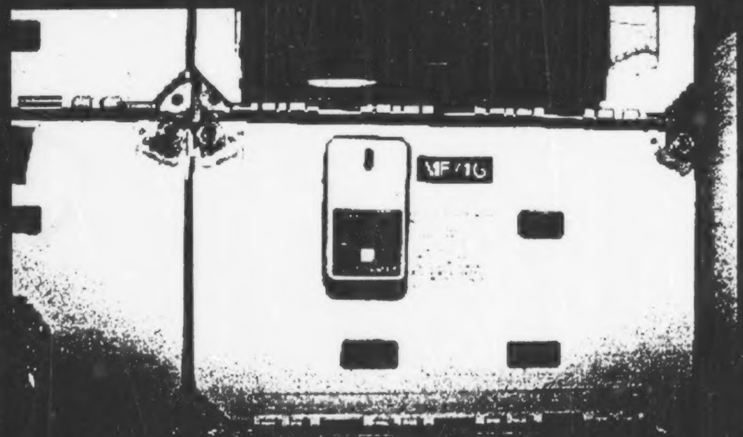
Air Quality Issue On 2A.1
ISS Mission

- Symptoms
  - The crew experienced adverse health effects o in the FGB while working in confined areas
- Conclusions
  - Symptoms most likely caused by inadequate ventilation at worksite
  - Recommended improvements for next flight include
    - Better ventilation
    - Real-time “worksite monitors to measure CO_2, dew point, and airflow”

Confined Work Areas on ISS

Infrared Based Carbon Dioxide Monitor is Selected

- CDU 440 (ISC) selected because of similarity of design and components to ISS CSA-CP



CSA-CP

Filter (water and particulates)

CDM

Results of CDU 440 Performance Tests

- Sensor noise: <20 ppm
- Response: 90% response in < 5 seconds
- Recovery: 90% in <10 seconds
- Temperature: Exposure to 0.1% and 2.00% CO_2 at 39°C resulted in - 0.01% and +0.1% absolute difference respectively-
- Interferences: Not to nominal spacecraft contaminants

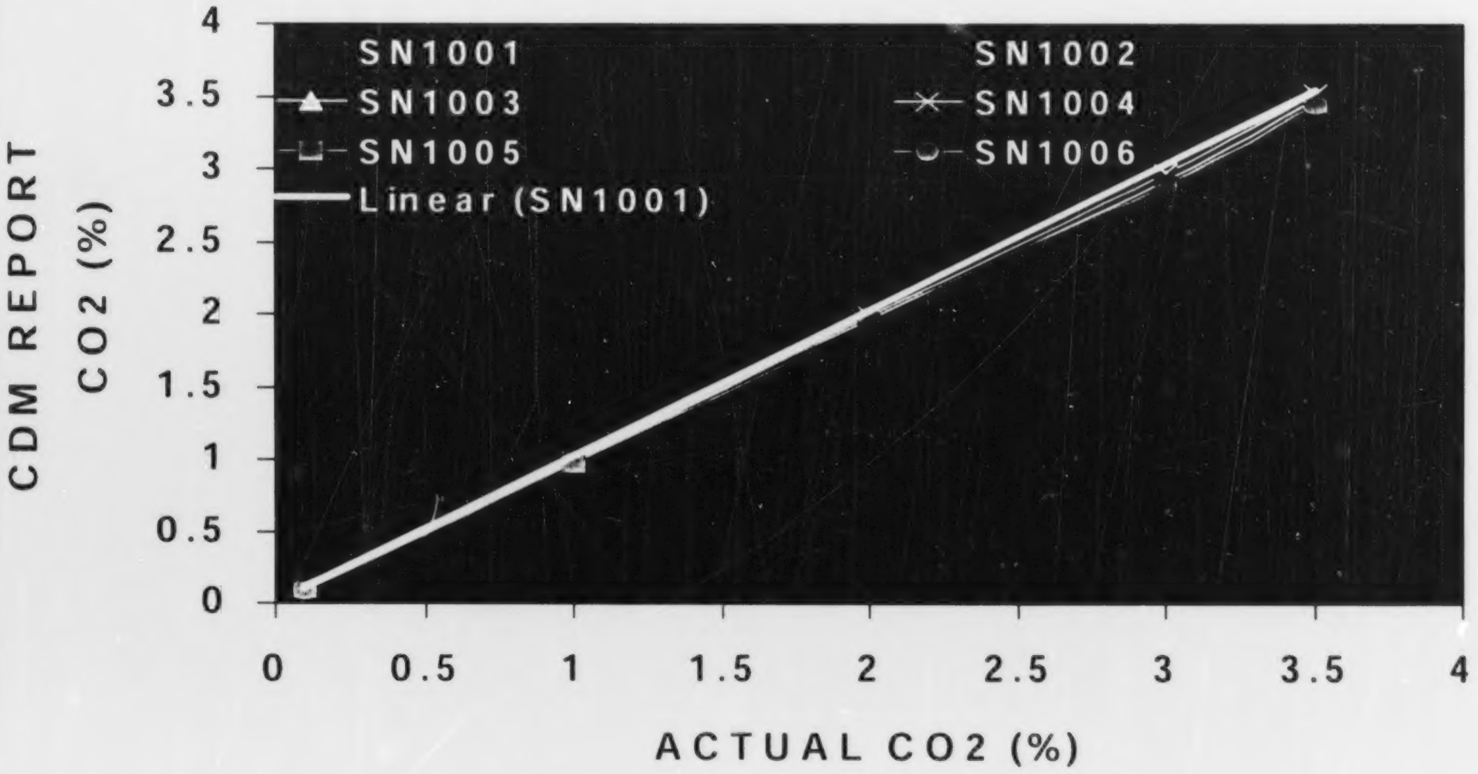
wyle laboratories

NASA

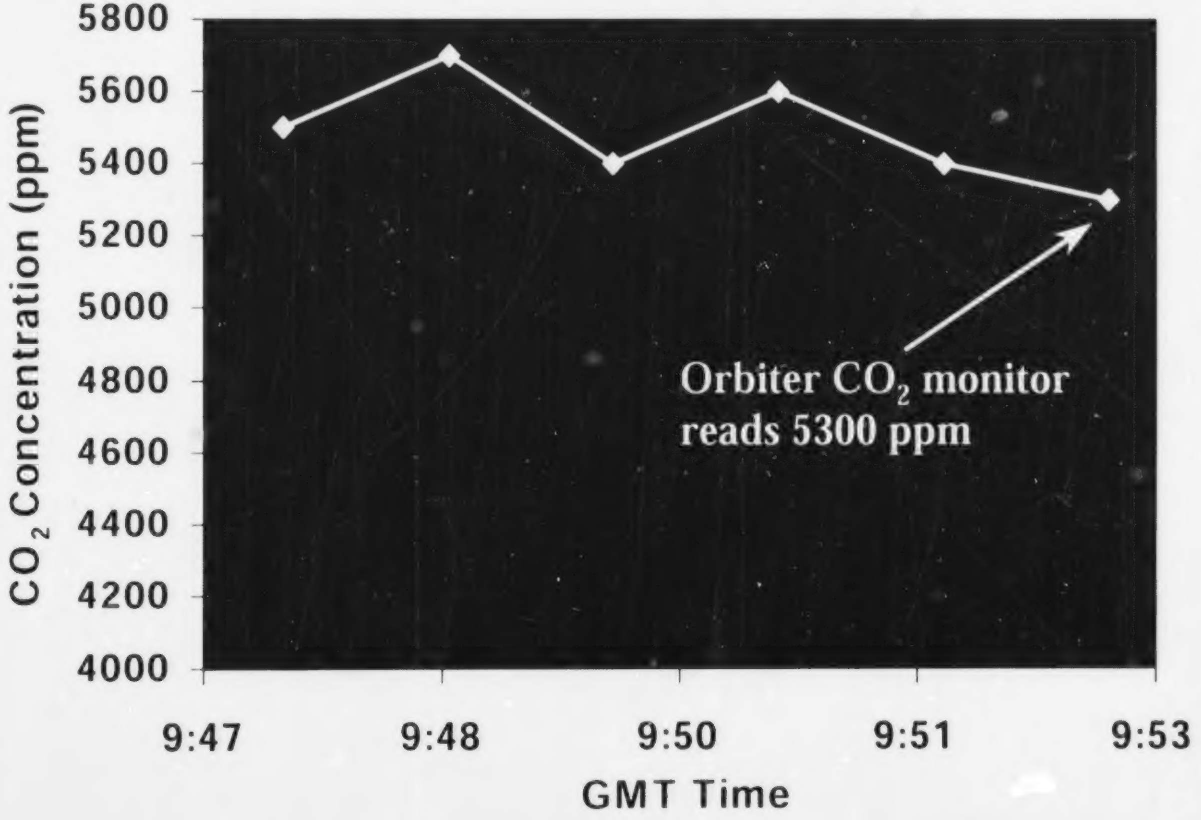
Results of CDU 440 Performance Tests

- Precision and accuracy testing easily met requirements for 6 units tested at 0.1% and 2% CO_2
- Humidity testing (25%-80% RH) at 1% CO_2 was successful
- Marked pressure dependency detected, but linear function
- Variation with pressure at high concentrations (5% CO_2)

Linear Range Determined For Six CDU 440s



CDM Data From STS-101
May 20, 2000



Orbiter CO_2 monitor reads 5300 ppm

Need for Volatile Organic Analyzer On ISS

- Longer missions and more limited escape options
- Detect accumulation of a volatile organic compound to unacceptable levels
- Monitor effectiveness of decontamination efforts following a contingency event
  - fire
  - spills/leaks

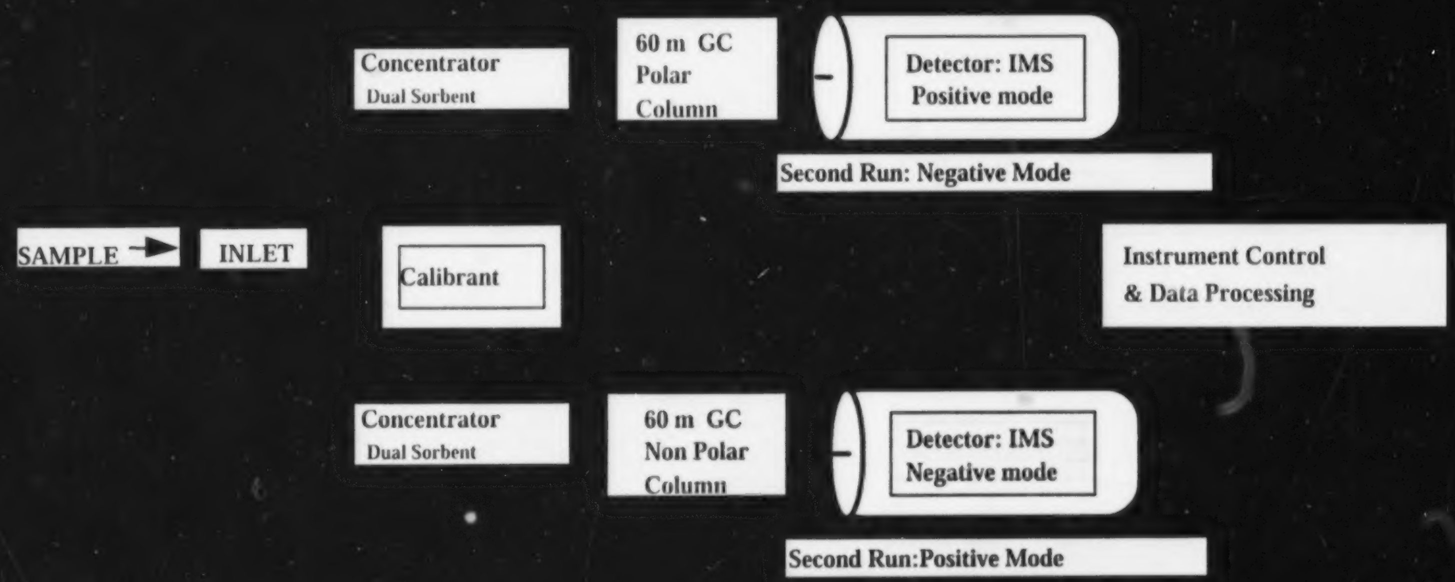
Volatile Organic Analyzer (VOA) Operational Requirements

- Periodic analysis target compounds in ISS air
- Diversity of target compounds and concentrations (see paper) in complex mixture
- Operate in contingency events
  - For example, provide data to help ground personnel and crew determine when to remove masks

VOA Performance Requirements

- VOA Specifications
  - Technology: Gas chromatography-ion mobility spectrometry (GC/IMS)
  - Weight: 44.5 kg Power: 1 amp@120vdc Gas: 4 hrs of 4ml/min nitrogen
  - Size: 48 cm x 27 cm x 71 cm (.09m^3 or 3.2 ft^3)
- VOA Performance Requirements
  - Operate in nominal and contingency conditions once per day for 5 years
  - Operate in changing pressure, temperature, and humidity
  - Atmosphere contains high levels of CO_2, CH_4, H_2, and water vapor

How the VOA Works



SAMPLE → INLET

Calibrant

Concentrator
Dual Sorbent

60 m GC
Polar
Column

Detector: IMS
Positive mode

Second Run: Negative Mode

Concentrator
Dual Sorbent

60 m GC
Non Polar
Column

Detector: IMS
Negative mode

Second Run:Positive Mode

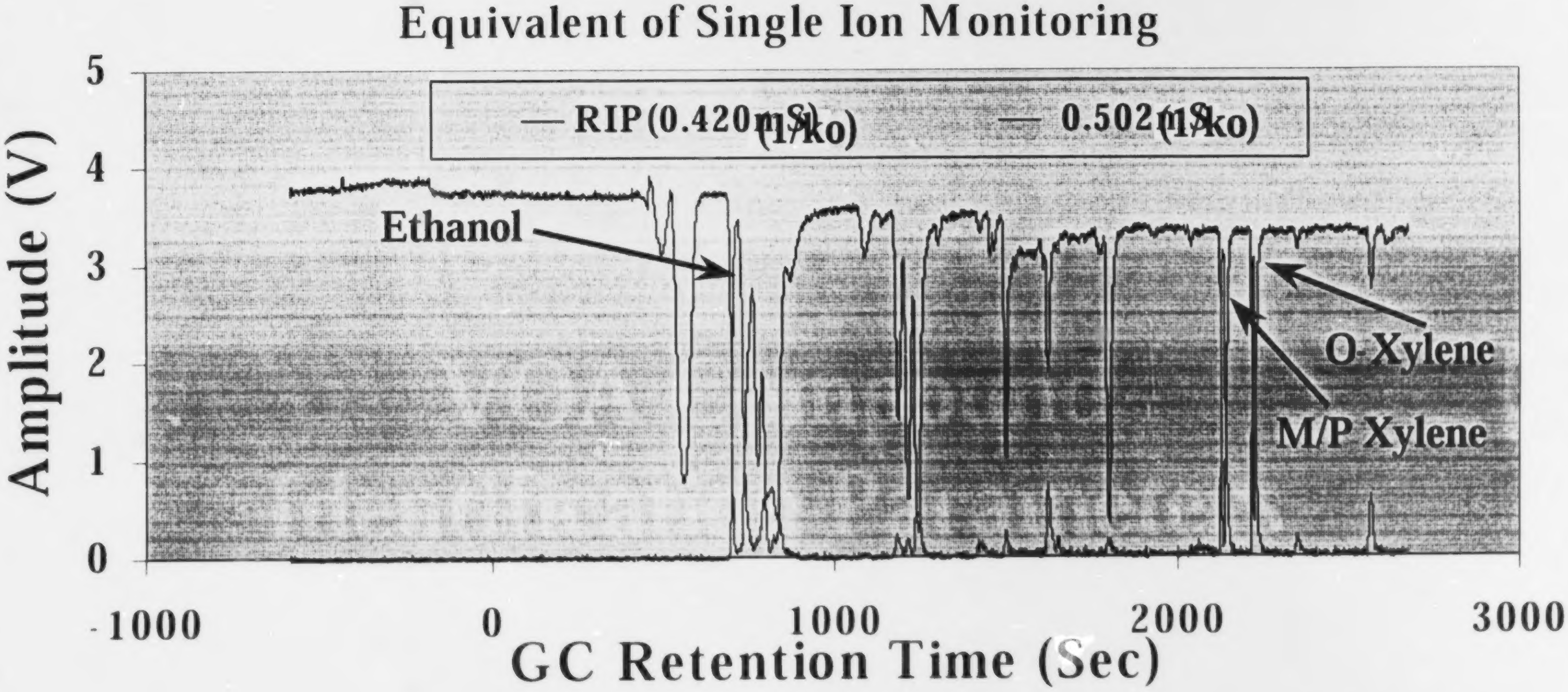
Instrument Control
& Data Processing

VOA
and VOA/RME On Orbit

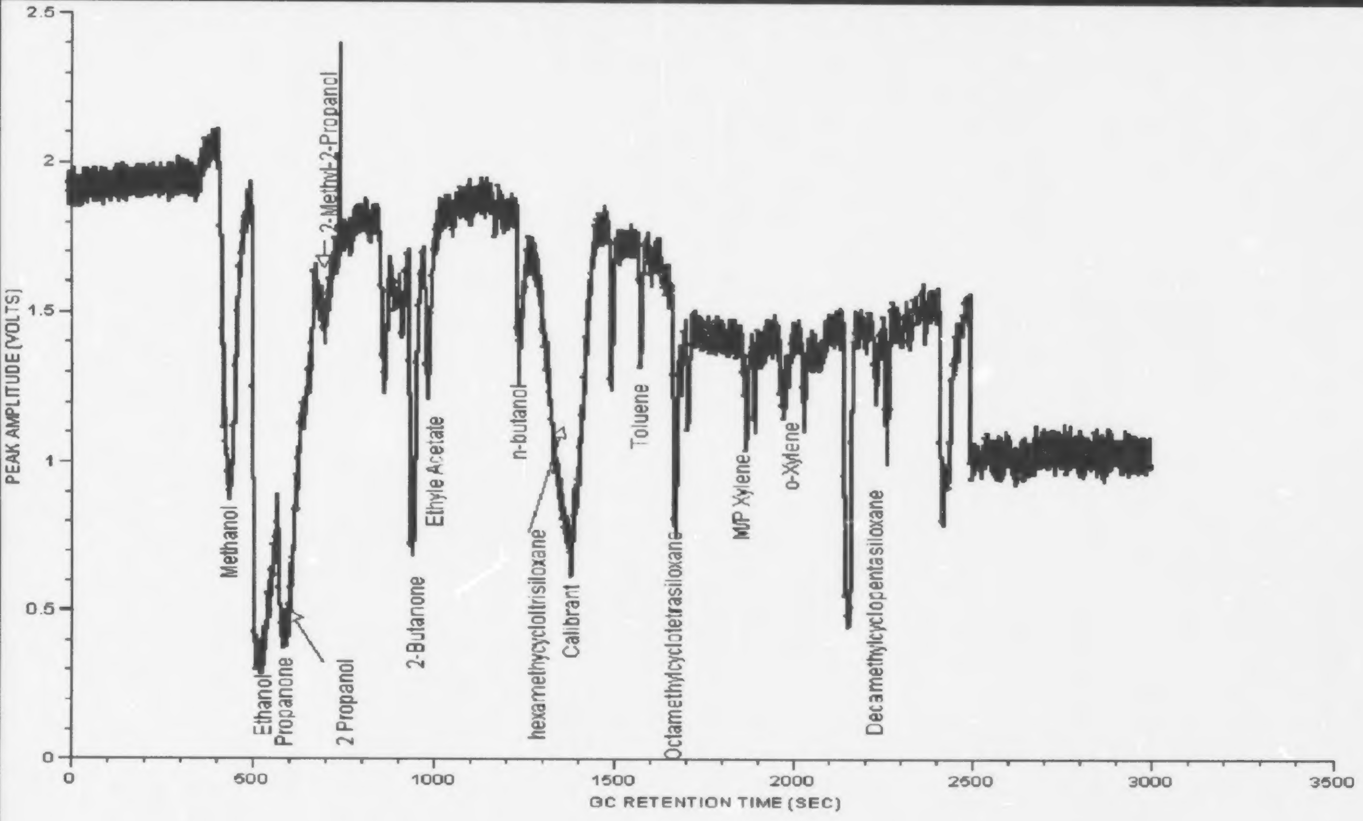
VOA on ISS rack

VOA/RME On Orbit
(STS-89)

VOA Compound Identification Parameters



STS- 89 VOA/RME
Positive Mode Run: Day 5



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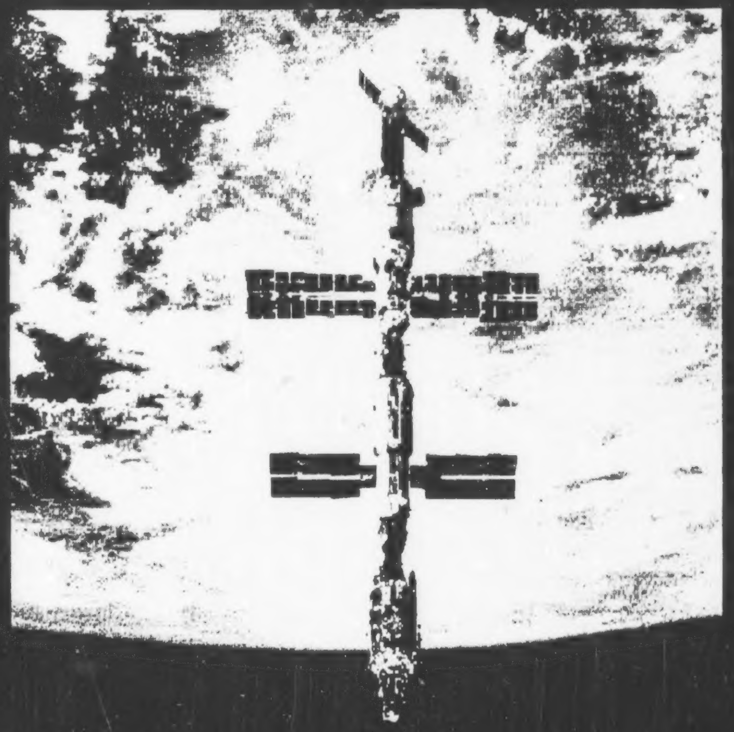
Advanced Work

- 2nd Generation VOA (2-5 years)
  - Assessing GC/IMS, FTIR, and MS technologies
- Derivative method being developed (UMIST) to analyze formaldehyde at ppb levels using current VOA
- Evaluating techniques for other reactive compounds, such as ammonia
- Assess ozone levels on spacecraft

Conclusions

- Experience from human spaceflight clearly shows air quality degradations will occur
- Synergy of toxicologists and chemists to develop requirements to select correct instruments
- A combination strategies and technologies is required to meet the scope of monitoring
- Requirements can change with spacecraft and mission

Tomorrow



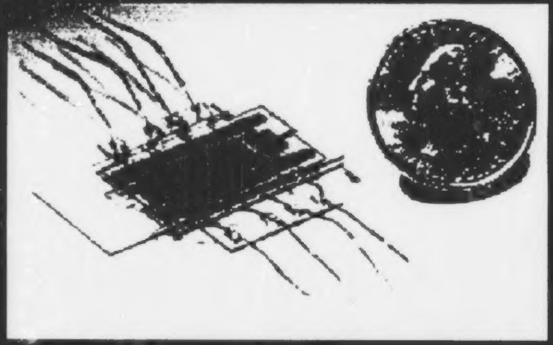
The Future at NASA
Miniaturization

E- NOSE

LAB ON
A CHIP

Preconcentrator/
Thermal Desorber
4 SAW
Array
One Meter
GC Column

IMS



CHARACTERIZATION OF AIR QUALITY ABOARD SPACECRAFT USING ARCHIVAL SAMPLERS

T. Limero, J. Boyd, M. Martin, P. Covington
(Wyle Laboratories)

John T. James (NASA/Johnson Space Center)

PRESENTATION OUTLINE

- ◆ Purpose for Archival Air Sampling
- ◆ Air Quality Degradation Incidents on Spacecraft
- ◆ Archival Samplers used on Spacecraft
- ◆ Preflight and On Orbit Use of Samplers
- ◆ Postflight Analyses of Samplers
- ◆ Advanced Work
- ◆ Future Work

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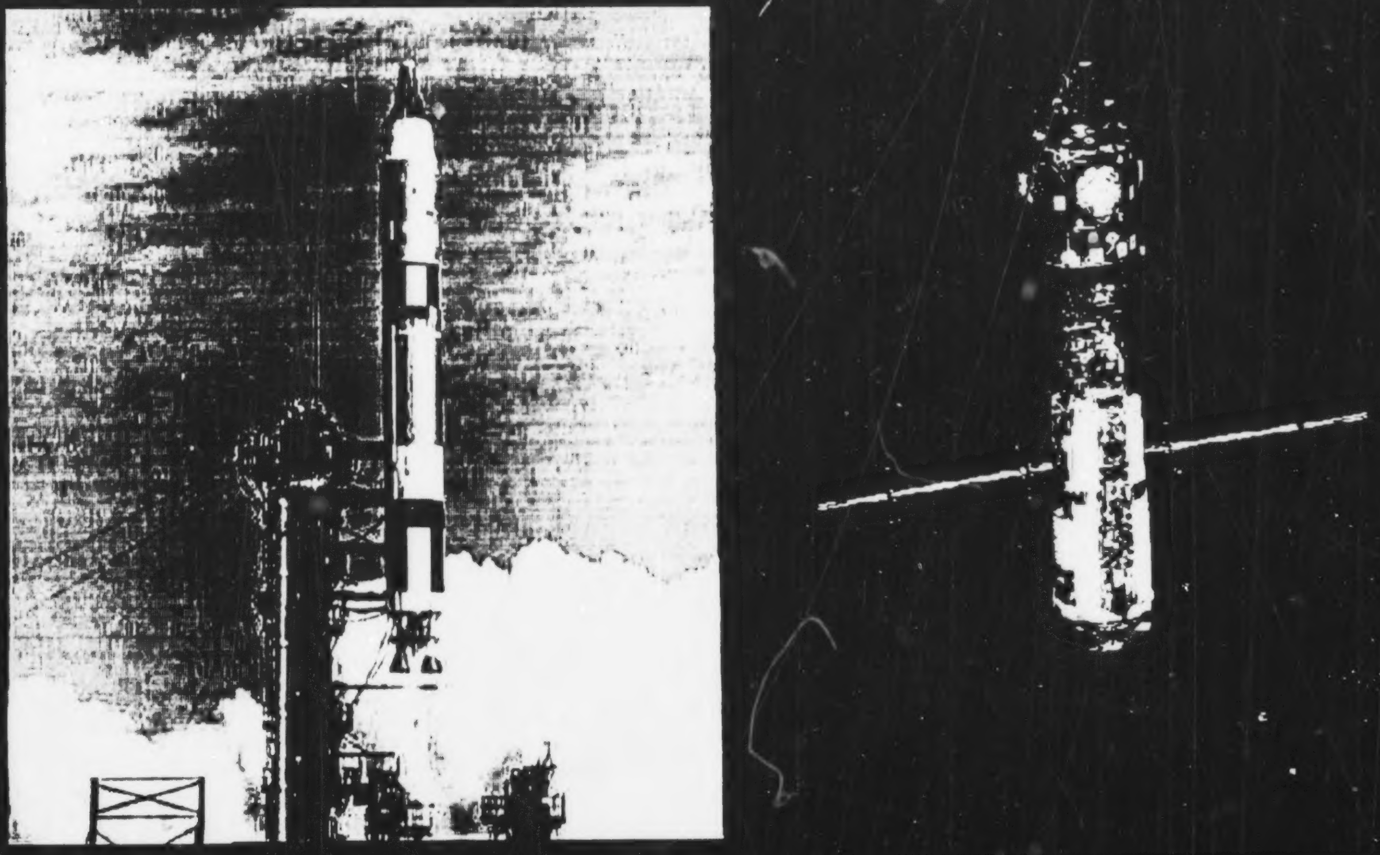
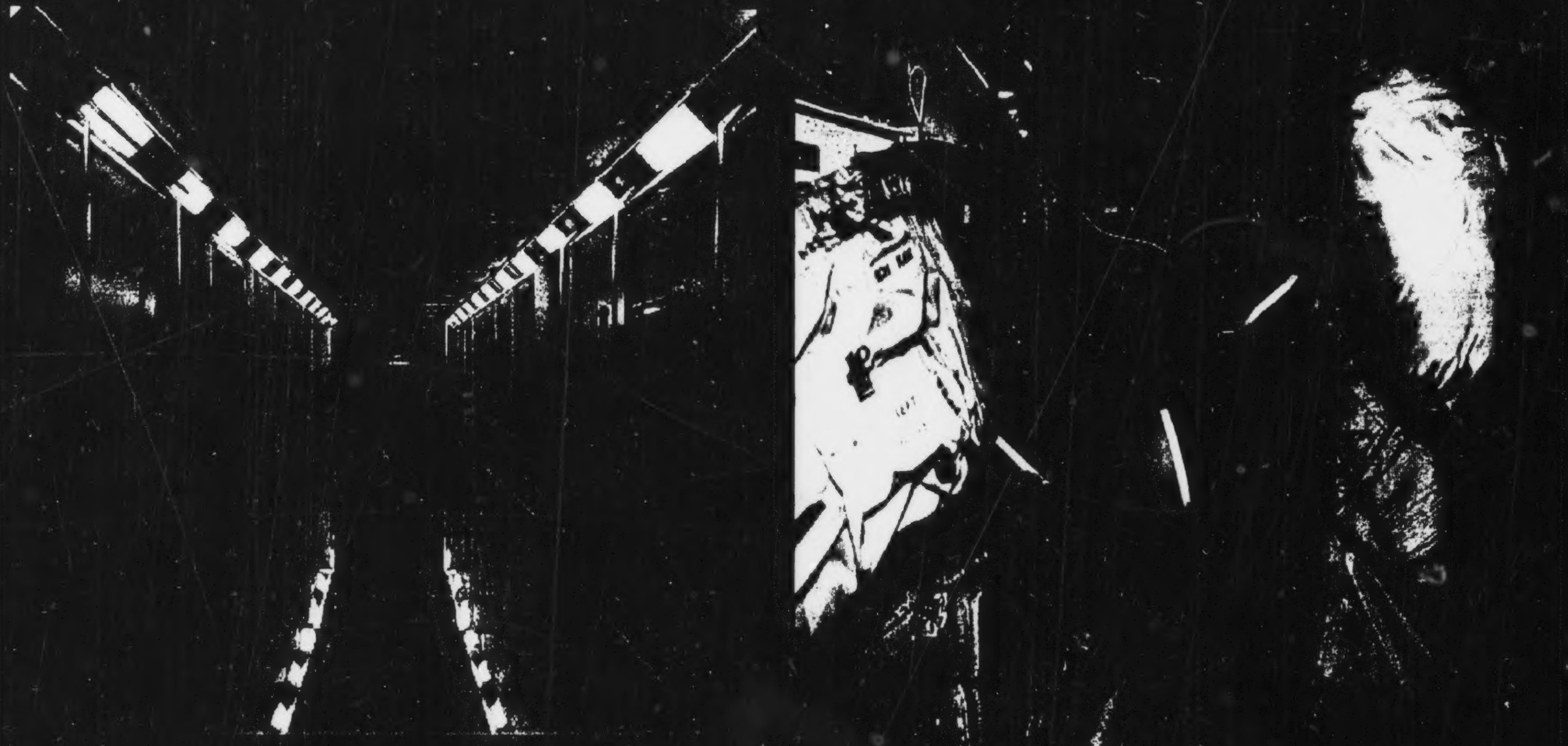
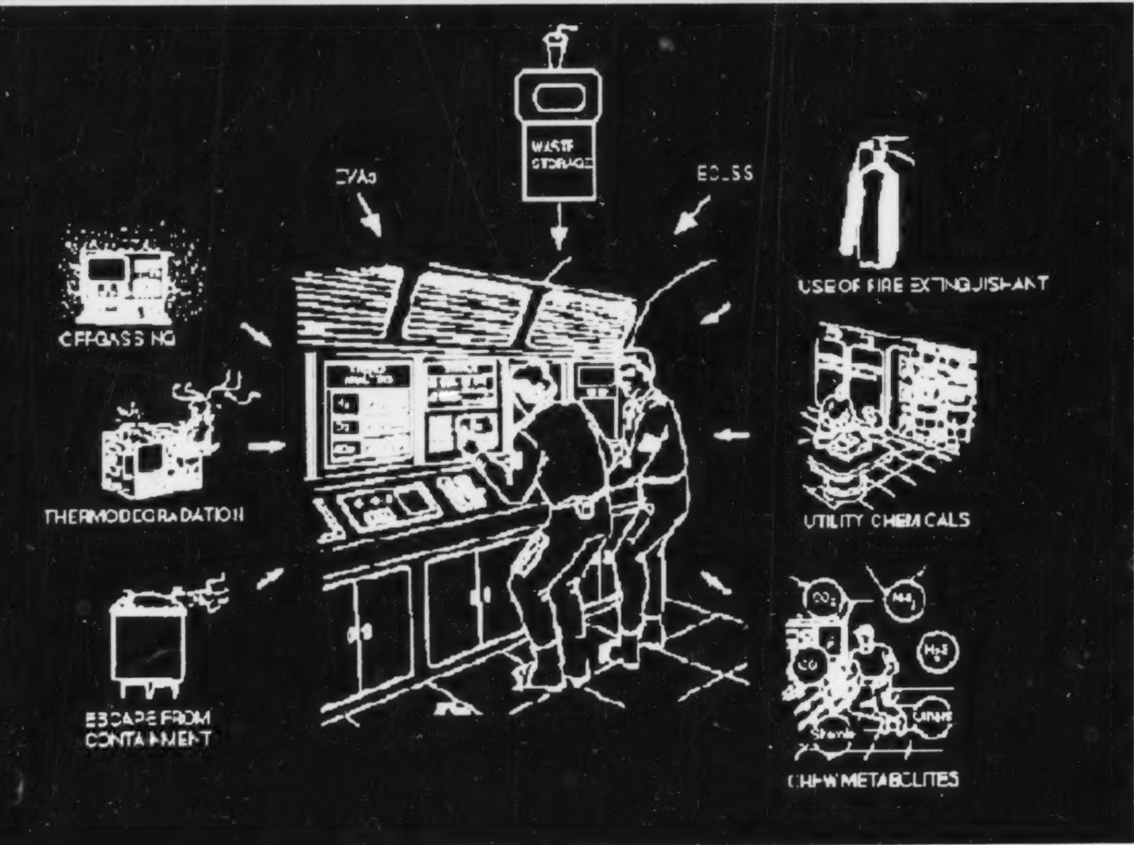
Archival Sampling From the Early Days of The Gemini Program to ISS



More Complex Spacecraft Representative Sampling Is an Issue



Sources of Air Contaminants on Spacecraft


WASTE STORAGE
EVAs
ECLSS
OFFGASSING
THERMODEGRADATION
ESCAPE FROM CONTAINMENT
USE OF FIRE EXTINGUISHANT
UTILITY CHEMICALS
CO2
NH3
H2S
CO
Urine
Stools
CREW METABOLITES

Why Sample VOCs On Spacecraft?

- ◆ Nominal Conditions On Spacecraft
  - Balance between generation and removal of volatile organics from ISS atmosphere
  - Air is renewed not replaced
- ◆ Purpose of VOCs Sampling on Spacecraft
  - Provide data that the environmental control and life support (ECLS) system functioned properly
  - Permanent record of air quality acceptability for crew health purposes
  - Verifies proper operation of real-time monitors

Why Sample VOCs On Spacecraft?

◆ Contingency events on Spacecraft
  - Slow accumulation of VOCs to unacceptable levels
  - Leak, spills, thermodegradations (fires)

◆ Purpose of Sampling VOCs
  - Identify contaminants and their concentrations released during the event
  - Verifies readings from real-time monitors
  - Documented means of assessing crew exposure to contaminants during and following the event

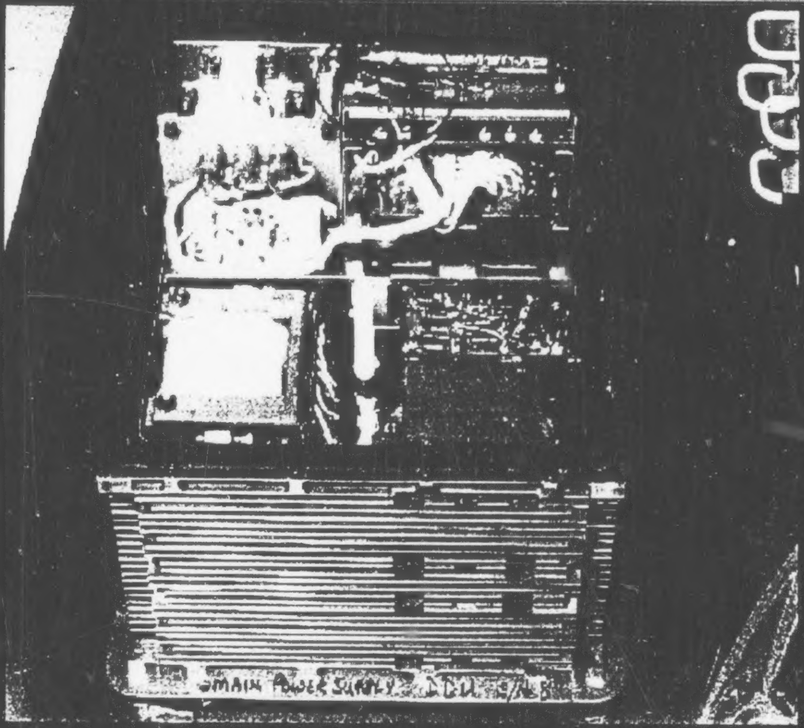
Air Quality Experiences On Shuttle

- ◆ Nominal
  - Generally good air quality (<15 mg/m^3 total VOCs)
- ◆ Contingency
  - Leaks and spills
    - – Fixative from experiments
  - Thermodegradation
    - – Overheated electronics
    - – Orbiter refrigerator/freezer (ORF) overheated fan

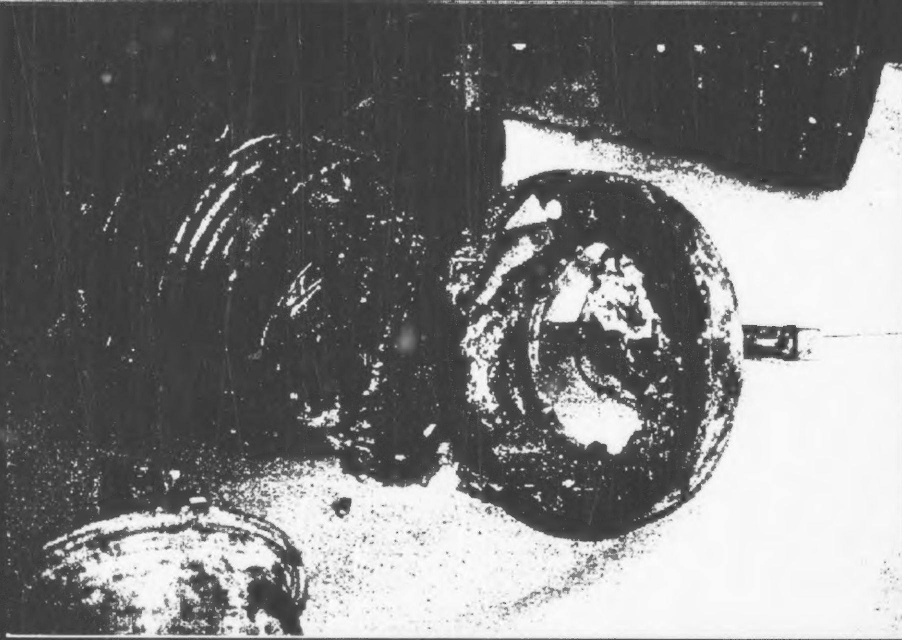
Air Quality Experiences
MIR Station

- Nominal
  - Unexpectedly good air quality for 10 year-old Mir
  - Unusual Freons (F82)
- Contingency
  - Leaks and spills
    - Ethylene glycol
  - Thermodegradation
    - Solid Fuel Oxygen Generator (SFOG)
    - BMP valve

Spacecraft Contingencies


MAIN POWER SUPPLY

Shuttle Overheated Electronics



MIR SFOG Component After Fire

Air Quality Experiences International Space Station

- ◆ Nominal
  - Air quality has been acceptable, although higher than expected concentrations of methanol and some alcohols. Also siloxanes levels are a concern
- ◆ Contingency events
  - Crew reported air quality issues on several missions
    - Symptoms related to stagnant air in localized areas
    - Persistent odors in modules

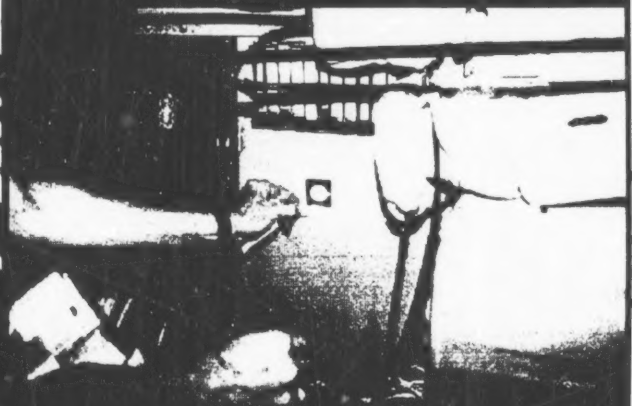
Objectives of Samplers

- Grab Sample Container (GSC)
  - Collect instantaneous sample of air in specific locations
  - Very volatile and less volatile compounds sampled
- Solid Sorbent Air Sampler (SSAS)
  - Collect 7 time-integrated air samples, usually 24 hours
  - Very volatile compounds (CO) are not sampled
- Formaldehyde Badge
  - Provides means to “fix”and transport formaldehyde sampled from the air for groundbased analyses

Archival Samplers on Orbit

GSC

SSAS



Formaldehyde
Badge

Preflight Preparation of Samplers

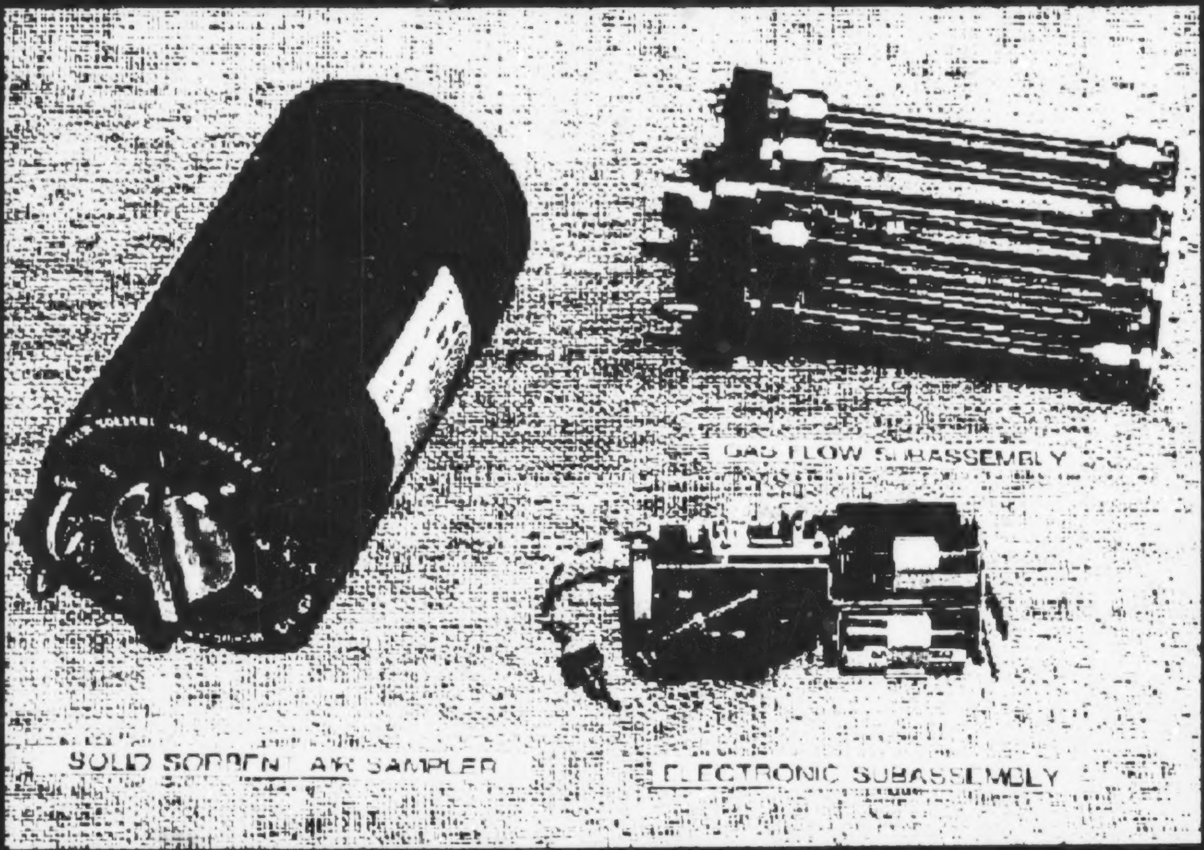
- GSC
  - 300 ml Summa^{tm} canisters are cleaned by cycles
    - Evacuation
    - Refill with humidified, zero air
    - Heat the canister in an oven at 50°C
  - Canisters are leak checked by helium backfill on vacuum rack
  - Proofed by GC/MS
  - Three surrogates are added to the GSC that span volatility and polarity range of sample compounds

GSC

Preflight Preparation of Samplers

- SSAS
  - Tubes contain mixture of Carboxen 569 and Tenax
  - All tubes are cleaned by heating with nitrogen flow
  - All tubes are proofed by GC/MS
  - Three surrogates added
  - At no time are tubes exposed to laboratory atmosphere
- Formaldehyde
  - Uptake rates are determined for each batch
  - Positive and negative trip controls are prepared

SSAS Components


GAS FLOW SUBASSEMBLY
SOLID SORBENT AIR SAMPLER
ELECTRONIC SUBASSEMBLY

On Orbit Sampling Regime

- Shuttle
  - Preflight GSC prior to crew loading
  - 2 GSCs and formaldehyde badges for each flight
  - SSAS manifested if Spacehab or Spacelab is on Shuttle
- ISS
  - Extensive assembly flight sampling: GSCs and formaldehyde
  - Increment crews: GSCs for 1 sample/month and contingencies
  - SSAS samples acquired in Service and Lab modules every 2 weeks
  - Formaldehyde badges deployed for 12 hours, once a month in Lab and Service module

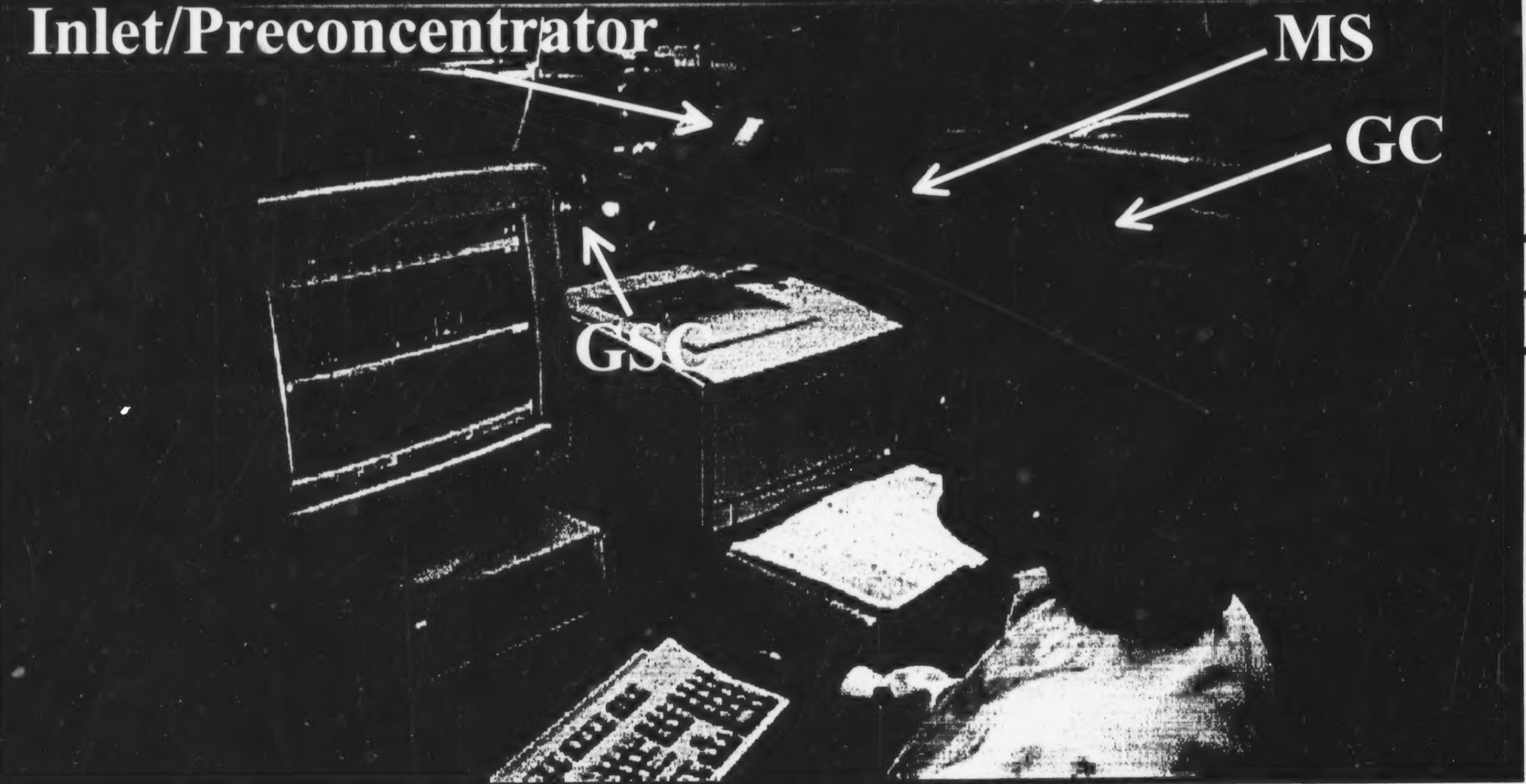
Postflight Analyses Requirements Overview

- ISO 9001 Work Instructions used for all analyses
- Stringent QA requirements insure validity of results
- EPA methods (TO-14 and TO-15) guide QA techniques for GSC and SSAS GC/MS analyses
- NIOSH Chromatropic Acid method is used for formaldehyde analyses

Postflight Analyses of Air Samples Collected by the GSCs

- GC
  - Carbon Monoxide by GC/HID
  - Carbon Dioxide and Hydrogen by GC/TCD
  - Methane and Ethylene by GC/FID
- GC/MS
  - Polar and nonpolar VOCs
  - Lab and Trip controls (unused GSCs), plus surrogate controls are analyzed at this time
  - Recoveries are measured from surrogate analysis
- GSC pressures are monitored to detect leaks

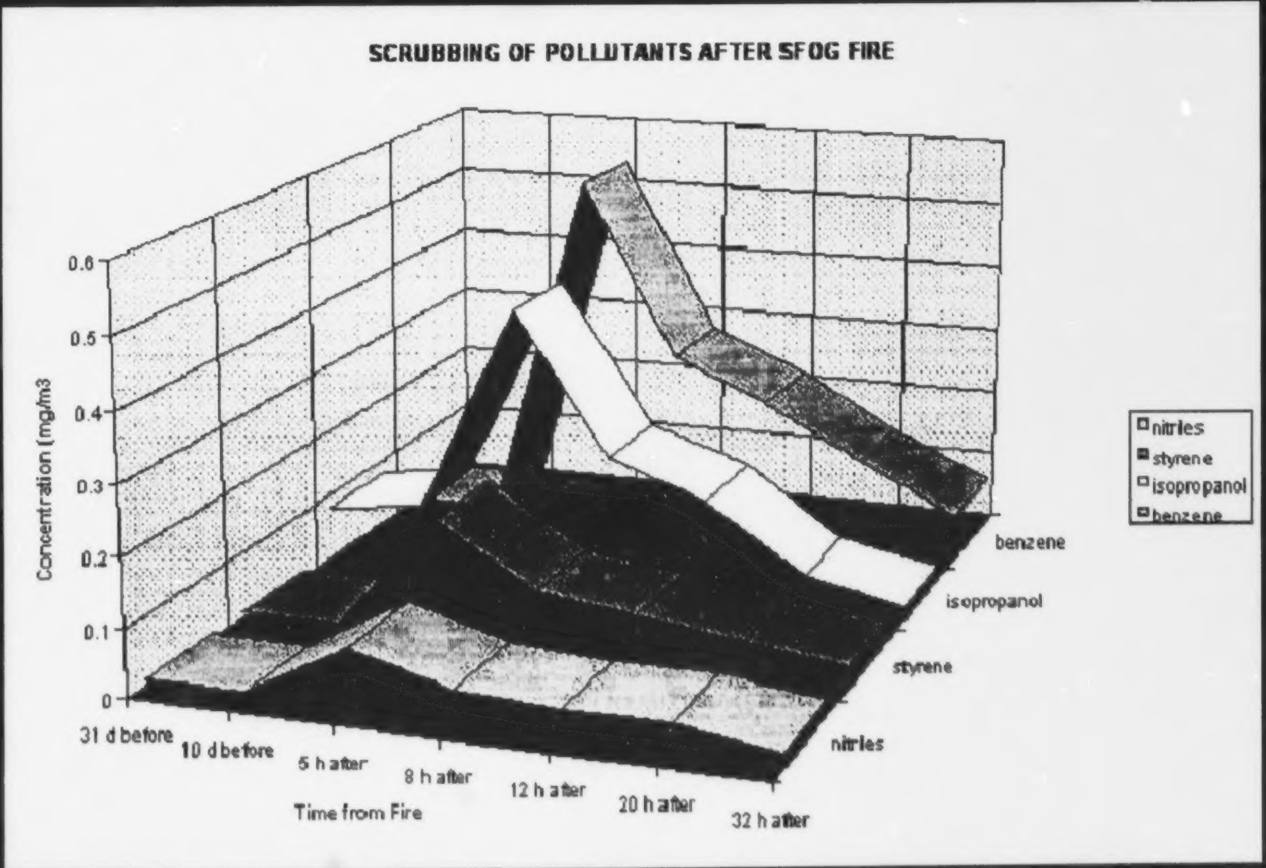
Laboratory Instrumentation for GSC and SSAS Analysis


Inlet/Preconcentrator
MS
GC
GSC

Postflight Analyses of Air Samples Acquired by the SSAS

- ◆ Thermal desorption of each tube into 500 ml GSC
  - Sample flow rate assessed compared to preflight flow
  - Water added to humidify before sample is added
  - Tubes are heated to 240°C with nitrogen flow
  - After desorption, GSC is pressurized to 1 atm.
- ◆ Samples run on GC/MS with archival GSC method
- ◆ Advantages of Desorption Technique
  - Tubes are never exposed to ambient air during ground ops
  - More sample available if the GC/MS fails during the run
  - Sample dilution can be used to bring compound into calibration range

Value of Archival Sampling in Mir Contingency

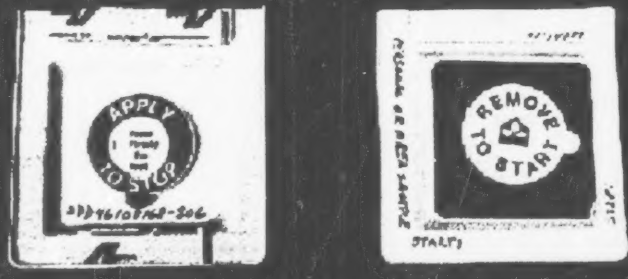


SCRUBBING OF POLLUTANTS AFTER SFOG FIRE

Postflight Analyses of Formaldehyde Badges

- Formaldehyde is “fixed” by sodium bisulfite
- Ground analysis begins with aqueous extraction of formaldehyde
- Chromatropic acid is added to solution to produce color
- Calibration curve is generated
- Color intensity is measured by a spectrophotometer to determine concentration

Start of Formaldehyde Postflight Analysis


APPLY TO STOP
REMOVE TO START

Badges

APPLY TO STOP

Removal of Disk with Formaldehyde

Typical Results From Archival Samplers

Compound	Avg. Concentration range (mg/m3)	MDL mg/m3	SMAC mg/m3
Formaldehyde	0.012-0.17 (0.93)	0.012	0.05
Methanol	Trace - 0.42	0.05	9
Ethanol	Trace - 2.6	0.05	2000
Acetone	Trace - 0.20	0.05	50
Isopropanol	Trace - 2.0	0.05	150
Dichloromethane	Trace - 0.10	0.05	50
Freon 113	Trace - 0.06	0.05	400
n-Butanol	Trace - 0.25	0.05	80
Toluene	Trace - 0.18	0.05	60
Methane	Trace - 29.0	6.6	3800
Hydrogen	Trace - < 3.3	0.41	340

Compound Range from some Shuttle and Mir flights

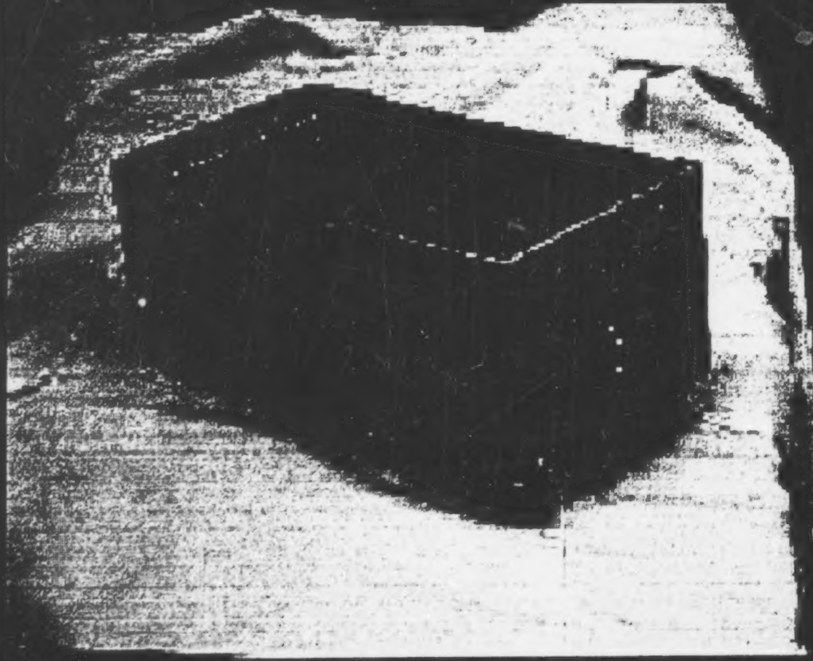
Advanced Work on Archival Analyses

- Respond to lessons from flight-Improve sampling in areas suspected of low air flow
- Evaluation of new inlet/preconcentrator for improved detection limits and sample separation
- Improved methods for high concentrations of alcohols
- Study of effectiveness of silicosteel canisters

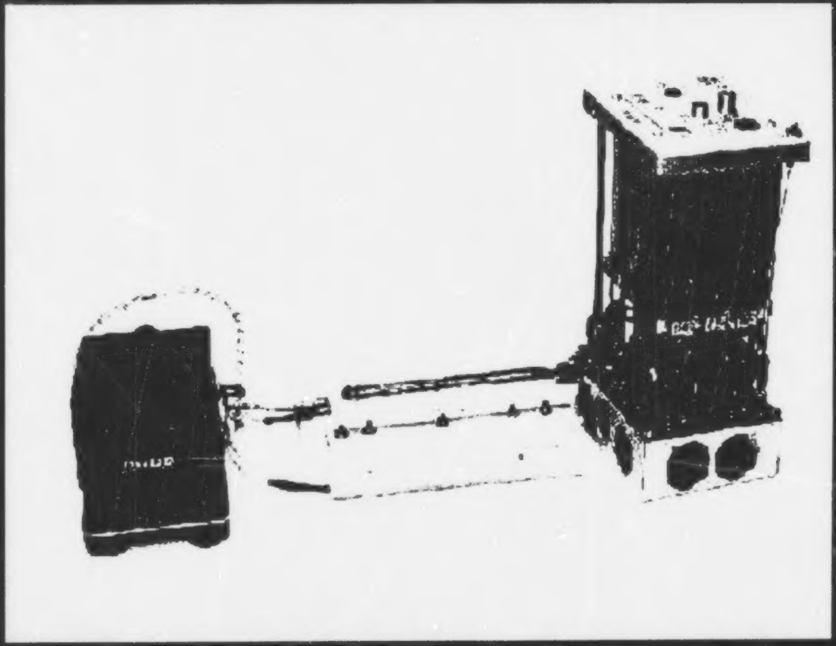
Advanced Work on Archival Analyses

- ◆ Automated Multisorbent Tube Air Sampler (AMTAS)
  - Preprogrammed for sample acquisition-crew only need deploy sampler, but contingency mode available
  - 16 tubes programmed to sample at set times
  - Reactive compounds might be sampled using special sorbents in 1 or more of the 16 tubes
  - Tubes are never exposed to laboratory air

AMTAS



AMTAS in Sample Mode

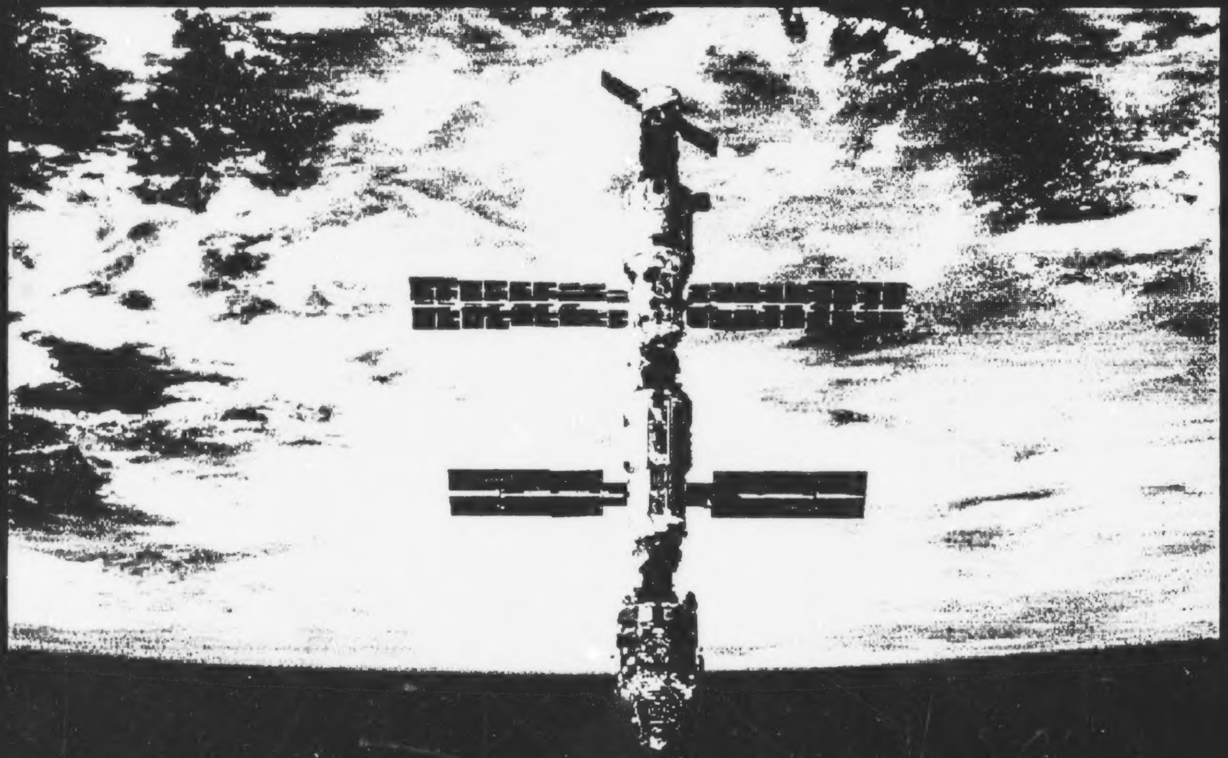


AMTAS in Desorb Mode

FUTURE WORK

- Automate Samplers where possible
- Miniaturize Samplers
- Improve analytical techniques to support miniaturized samplers
  - Improve methods and equipment to handle smaller samples
  - Improve method detection limits

ISS Today



RN Submarine Atmosphere Monitoring

- Retrospective Analysis

by Alex Goodall Submarine Environmental Chemistry Adviser
& Steve Moore Senior Occupational Hygienist

Ministry of Defence (Navy)
Institute of Naval Medicine
Alverstoke, Hants UK

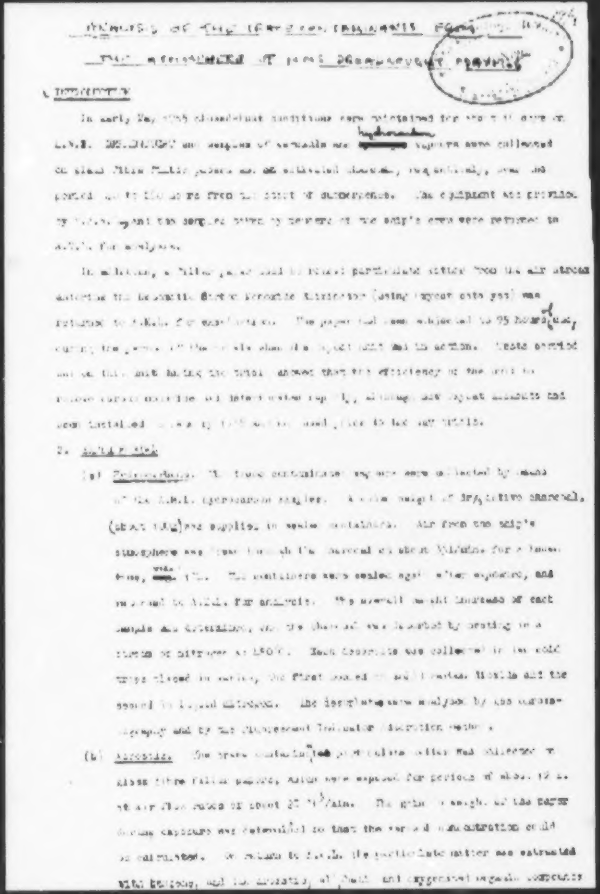
~ 40 years' atmosphere sampling

• HMS DREADNOUGHT	1963
• Early VALIANT Class	1960s
• RESOLUTION Class (Polaris boats)	1960s
• Later VALIANT Class	1970s
• SWIFTSURE Class	1970s
• TRAFALGAR Class	1980s
• VANGUARD Class (Trident boats)	1990s

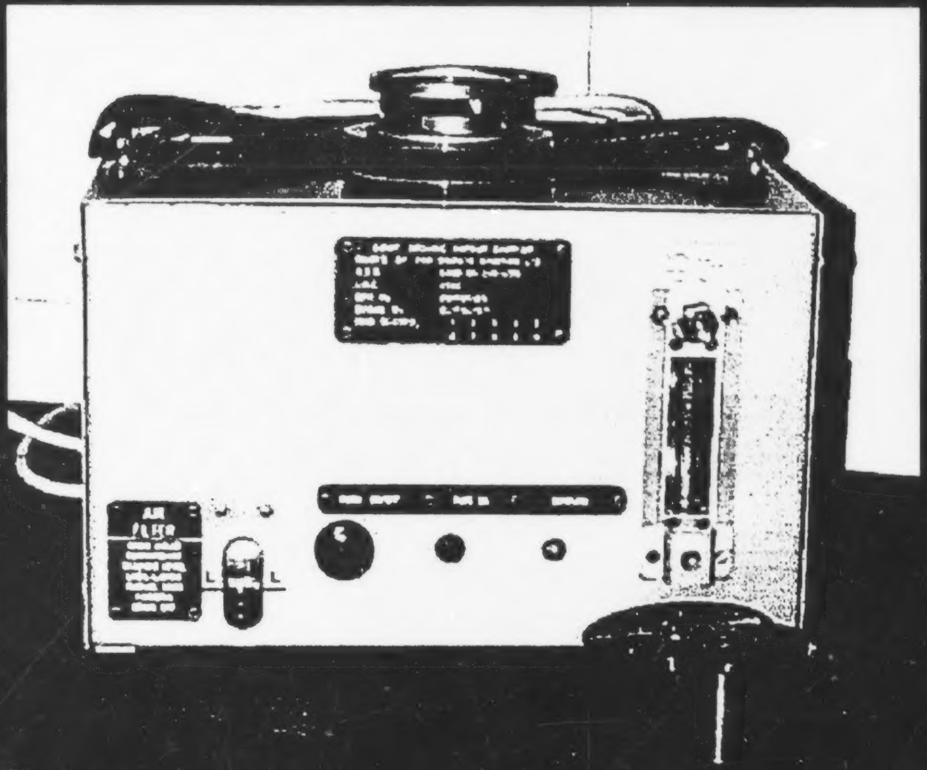
The early days

- Organic vapours
  - benzene, toluene, xylenes, C8 & C9 aliphatics, C9 aromatics
- Aerosol
  - total aerosol
  - total organic
  - aliphatic, aromatic & oxygenated organics

"Analysis of the Trace Contaminants from the Atmosphere of HMS DREADNOUGHT. May 1965"

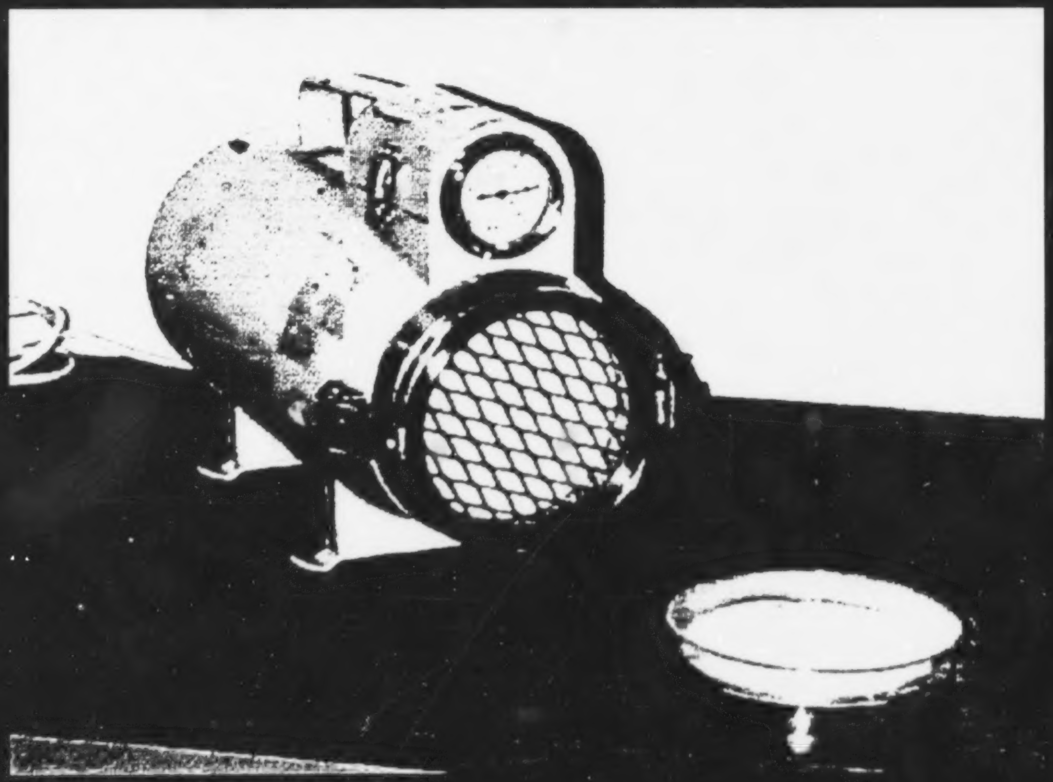


Organic vapour sampling using charcoal



100 g of charcoal for 12 hours at 35 lpm

Aerosol sampling using glass fibre filter



Glass fibre filter for 12 hours at 570 lpm (410 m^3)

Today - 24 hours at 700 lpm (1000 m^3)

Results

- Organic vapours
- 33 - 61 mg/m^3 Average: 44 mg/m^3
- Recommended maximum = 40 mg/m^3
- With uncertainties, possibly 78 mg/m^3
- 70% aromatics - xylenes 35%
  - **Benzene, toluene, methyl ethyl benzene**
  - **1,3,5- & 1,2,4-trimethylbenzenes, p-cymene**
- 30% C6 to C8 aliphatics

Results

- Aerosols
- 0.17 - 0.30 mg/m^3 Average: 0.2 mg/m^3
- 65% benzene-soluble material (aliphatics)
- Regarded as 'satisfactory'

The early 1980s

- Organic vapours
  - Total hydrocarbons
  - Individual aromatic hydrocarbons:

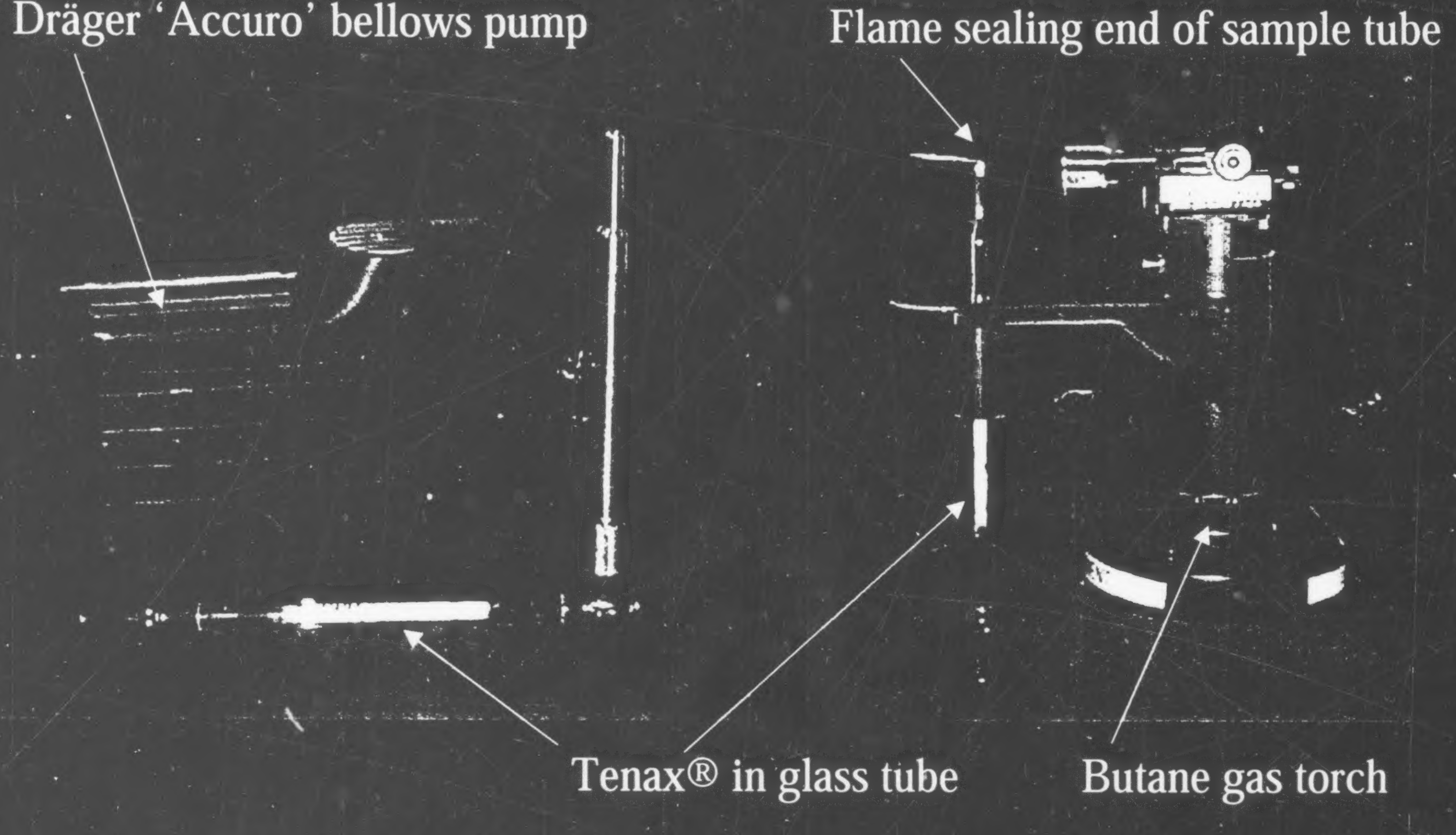
    benzene, toluene, ethylbenzene, xylenes, cumene, n-propylbenzene, o-ethyltoluene, m-ethyltoluene, mesitylene, p-cymene, pseudocumene, 1,2,3-trimethylbenzene, p-dichlorobenzene
  - Total aromatics
  - Total aliphatics
  - Total significant unknowns

The early 1990s

- Aerosols
  - Total aerosol
  - Metals analysis
  - Microscopic examination
- Organic vapours
  - New sampling technique under development
    - absorb more organic species than charcoal
    - automated analysis
    - lower limits of detection - shorter sampling time
    - easy to use by submarine crew
  - Tenax® TA - 200 ml hand-pumped sample

(Tenax is the registered trademark of the Enka Research Institute)

Tenax® organic vapour sampling kit


Dräger 'Accuro' bellows pump
Flame sealing end of sample tube
Tenax® in glass tube
Butane gas torch

Today

- Aerosols
  - **Total aerosol**
  - **Metals analysis**
    - **antimony, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, tin, titanium, vanadium**
  - **Total toluene-soluble material**
  - **Water-soluble anions analysis**
    - **fluoride, chloride, chlorate, nitrite, nitrate, bromide, sulphate, phosphate**
  - **Microscopic examination**

Today

- Organic vapours
    - Tenax® sampling replaced charcoal
    - 32 specific analytes
    - 26 others frequently found

Results

- Aerosols
- Reduced to 1/3 that of DREADNOUGHT
- 0.05 - 0.11 mg/m^3
- MPC 90: 0.5 mg/m^3

- Organic vapours
- Reduced to 1/5 that of DREADNOUGHT
- 6.8 - 15.2 mg/m^3
- MPC 90: 40 mg/m^3

Purpose of Retrospective Sampling

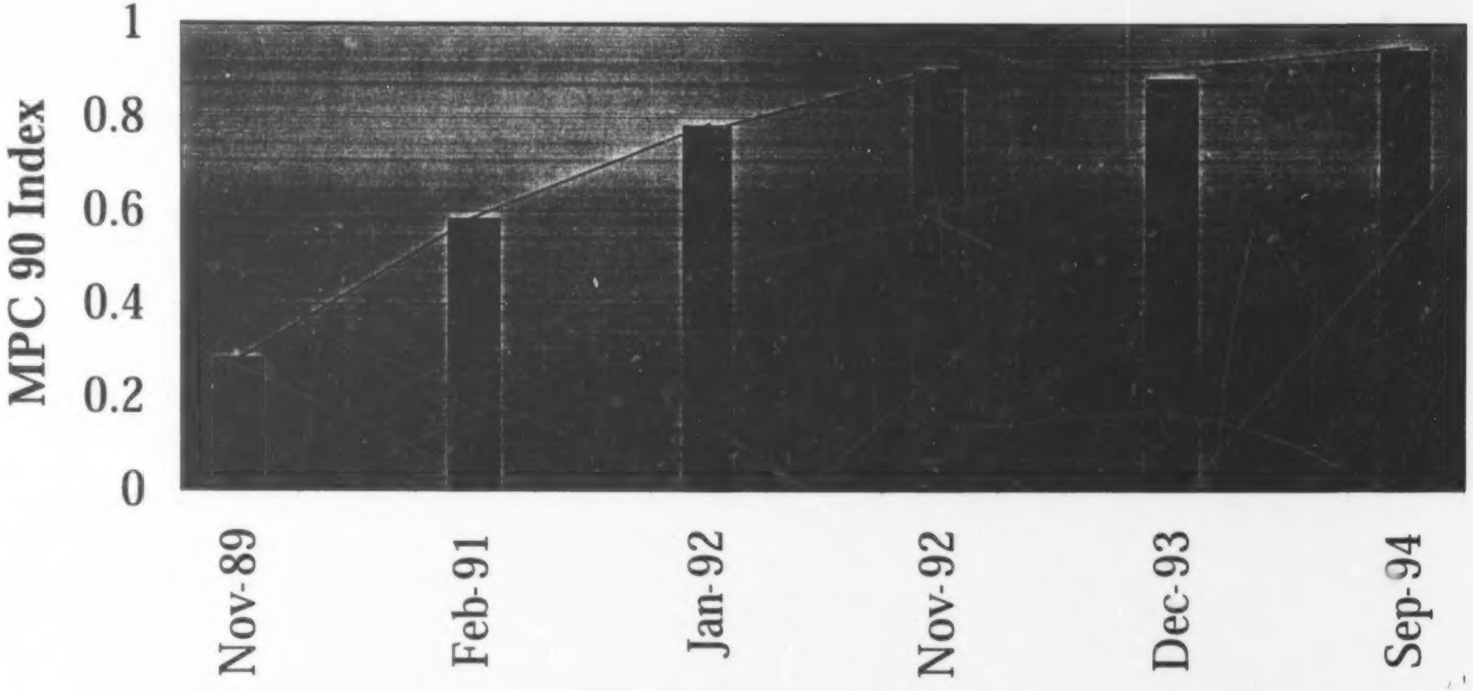
- To check compliance with MPCs
- To indicate trends

Summary of Results

- MPC excursions used to be frequent but now rare
- atmospheric quality varies greatly during a patrol
- atmospheric quality decreases with age of boat
- most important factor affecting atmospheric quality is good maintenance of air purification systems

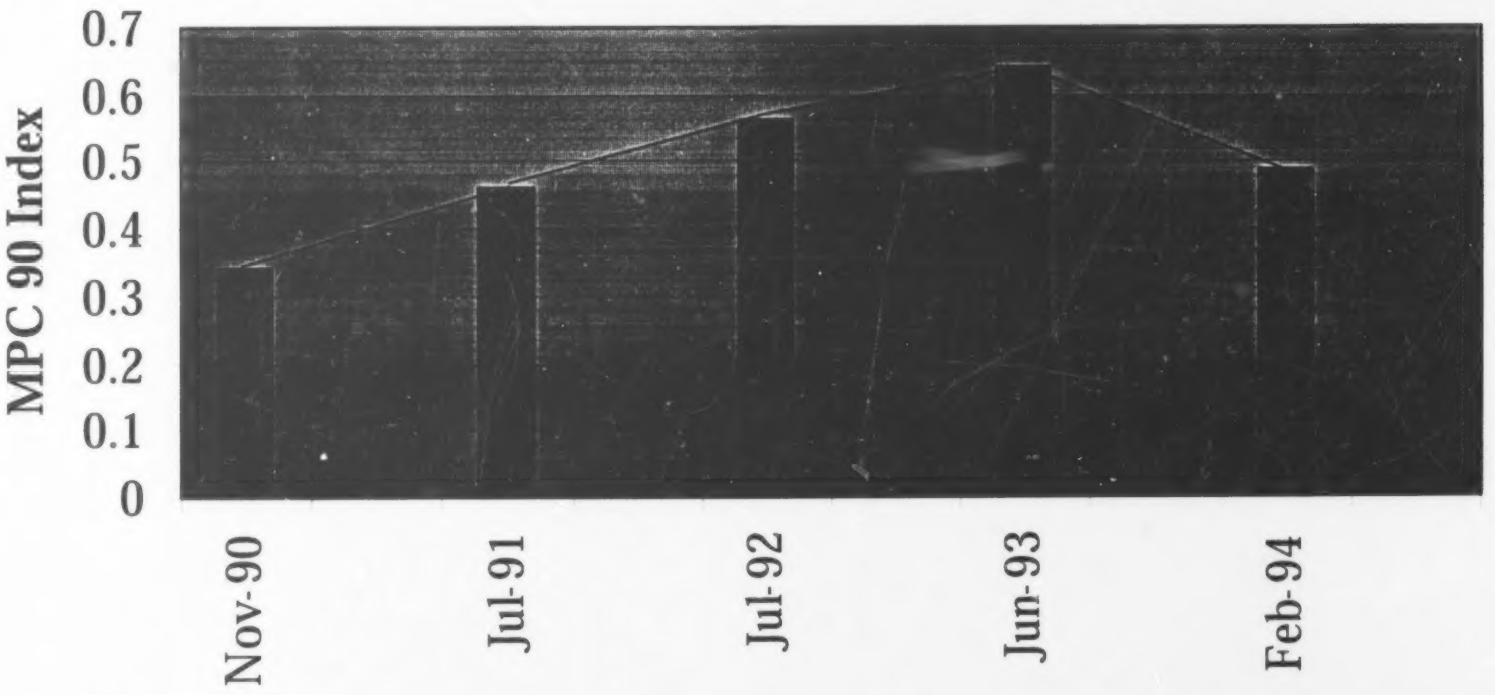
POLARIS Boat - Aerosol Trend Data

Port Crew



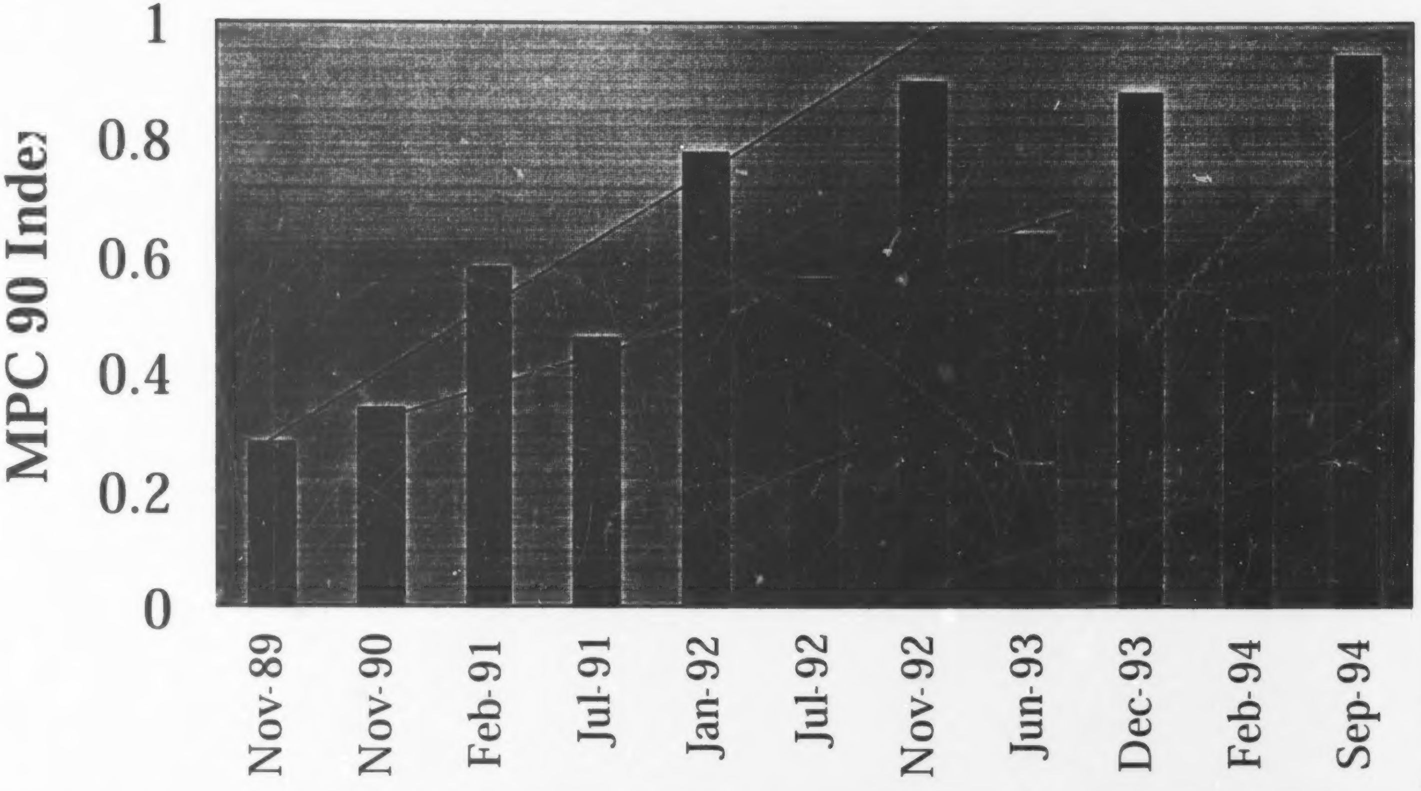
POLARIS Boat - Aerosol Trend Data

Starboard Crew



POLARIS Boat - Aerosol Trend Data

Port and Starboard Crews



I.N.M.
E MARI AD SALUTEM

ASSESSING FOETOTOXICITIY IN THE SUBMARINE ENVIRONMENT

Report of a Study by the Institute of Naval Medicine

Surgeon Lieutenant Commander
Graeme NICHOLSON Royal Navy
Institute of Naval Medicine

INTRODUCTION

Women have served at sea on RN surface ships for 10 years.

Other nations have women serving in conventional submarines

What risks would an unborn child be placed at by its mother serving in an RN submarine?

CURRENT STATUS

- RN has 16 nuclear powered submarines
- Stay at sea for up to 90 days
- Air purification equipment:
    - replenishes Oxygen
    - removes Carbon dioxide and monoxide
    - filters and precipitates aerosols and hydrocarbons
- However atmosphere profile still unlike 'outside world'

CURRENT CONTROLS

Health based occupational limits

set by extrapolation from occupational exposures

Set for males, not including foetotoxicity

Monitored by fixed onboard analysers, portable instruments and retrospective sampling

Compliance assessed by retrospective analysis of reports

PREGNANCY

Ovulation occurs around 14 days post menstruation.

Fertilisation and egg implantation occur within a few days of ovulation

Therefore a woman may proceed to sea BEFORE she is aware she is pregnant.

FOETOTOXICITY

Exposures may cause developmental abnormalities

Foetus most sensitive to chemical exposures, infections e.t.c. between 14 and 40 days post fertilisation.

Most abnormalities NOT due to environmental exposures

Late more subtle effects of exposure

TOXICITY STUDIES

Animal Studies
- may use high dose exposures
- may use unusual exposure routes

Epidemiological studies
- limited number of exposure chemicals
- difficulties defining end point

Limits usually extrapolated from animal study

STUDY AIM

The aim of the INM study was to assess the risk to the foetus from ionising radiation and chemical exposures inherent in the submarine environment to determine if a categoric assurance can be given to a woman serving in submarines that there is no additional risk to their unborn child.

ASSESSMENT

Legal implications:

- Health & Safety vs Equal Opportunities

Strategy

divide topics into:

- CO2 and CO - raised ambient atmospheric levels
- Other contaminants
- Radiation exposure

ASSESSMENT

Searches in:

- Toxicology text books
- Toxicology journals
- CD-ROM databases
- UK H&S Executive publications
- ACGIH publications

UN, ICRP and NRPB radiological information

ASSESSMENT

EH 40/97 Occupational Exposure Limits	HSE
HSE Guidance Notes EH 40/97	HSE
Threshold Limit Values TLV/BEI 96	ACGIH
Reproductive Hazards of Industrial Chemicals	Barlow SM et al
Toxicology and Industrial Health	Hayden LJ et al
Mutation Research	Gerber GB et al
Reproductive Toxicology	Ernhart CB
REPROTOX ® System on CD-ROM	Micromedex Inc
Hazardous Substances Data bank on CD-ROM	Micromedex Inc
MEDITEXT ® Medical management on CD-ROM	Micromedex Inc
Shepard's Catalogue of Teratogenic Agents on CD-ROM	
Recommendations of the ICRP No 60	Annals of the IRCP
Genetic and Somatic effects of Ionising Radiation	UNSCEAR

CARBON DIOXIDE (CO2)

CO2 levels usually 10 time normal atmosphere

Animal models show single day exposure to 6% CO2 cause increased risk of cardiac abnormalities in rats.

No long term chronic exposure data

No routine exposure or emergency limits set.

CARBON MONOXIDE

CO levels similar to those found in a smokers home.

UK Advice: Maternal carboxyhaemoglobin limit of 2.5% for general population

Ratio of Maternal CO to Foetal CO 1:1.1

Coburn equation allows calculation of limits in air

MPC changes possible and achievable

OTHER CONTAMINANTS

Large number of detected and potential low level contaminants

Which to assess?

1. Do existing / proposed MPCs protect the unborn child?
2. When an exposure standard exist does the substance have foetotoxic effects, and is it seen in the submarine environment?
3. Are compounds 'significant' contaminants?

OTHER CONTAMINANTS

Significant:

- Seen in retrospective sampling or specialist sampling performed for RN or USN
- Seen at levels greater than 1000 nanograms per cubic metre:

Mixed Aerosols assessed separately

OTHER CONTAMINANTS

87 substances eventually reviewed.

2 require downwards revision of MPC 90

9 require revision of emergency exposure limits (MPC 60 and 24)

9 potential foetotoxic substances were discovered with no MPCs

11 further substances with insufficient data to assess (including Nitrogen Dioxide)

AEROSOLS

Produced from cooking, hot machinery and smoking

Contain Polycyclic Aromatic Hydrocarbons (PAHs)

Similar levels to a smokers house

Passive smoking leads to increased risk of low birth weight and spontaneous abortion

RADIATION

Assessment of dosimetry records undertaken

Dose rates below those set by IRCP and NRPB for exposure of pregnant women

Should be excluded from being Classified Workers as:

- highest dose group
- potential for exposure to unsealed sources
- one of limited pool of workers

CONCLUSIONS

Categoric assurance on Radiation Safety

No categoric assurance on atmospheric contaminants

Some areas may be resolved by changes of MPCs

Some major areas have insufficient data to allow complete assessment (CO2 and NO2)

ACKNOWLEDGEMENTS

The INM Report on which this paper is based: 'Mixed Manning In Submarines: Foetal Health' was authored by Surgeon Commodore GHG McMillan Royal Navy, Medical Officer in Charge at INM.

The subject reviewers were:

Surgeon Commander M Dean Royal Navy, Mr A Brittain, the Division Toxicologist and Mr J Holden, Head of Health and Hygiene Division and Surgeon Commander DC Brown Royal Navy, Defence Adviser in Radiation Medicine.

On board trial [illegible] regenerative carbon [illegible] scrubber

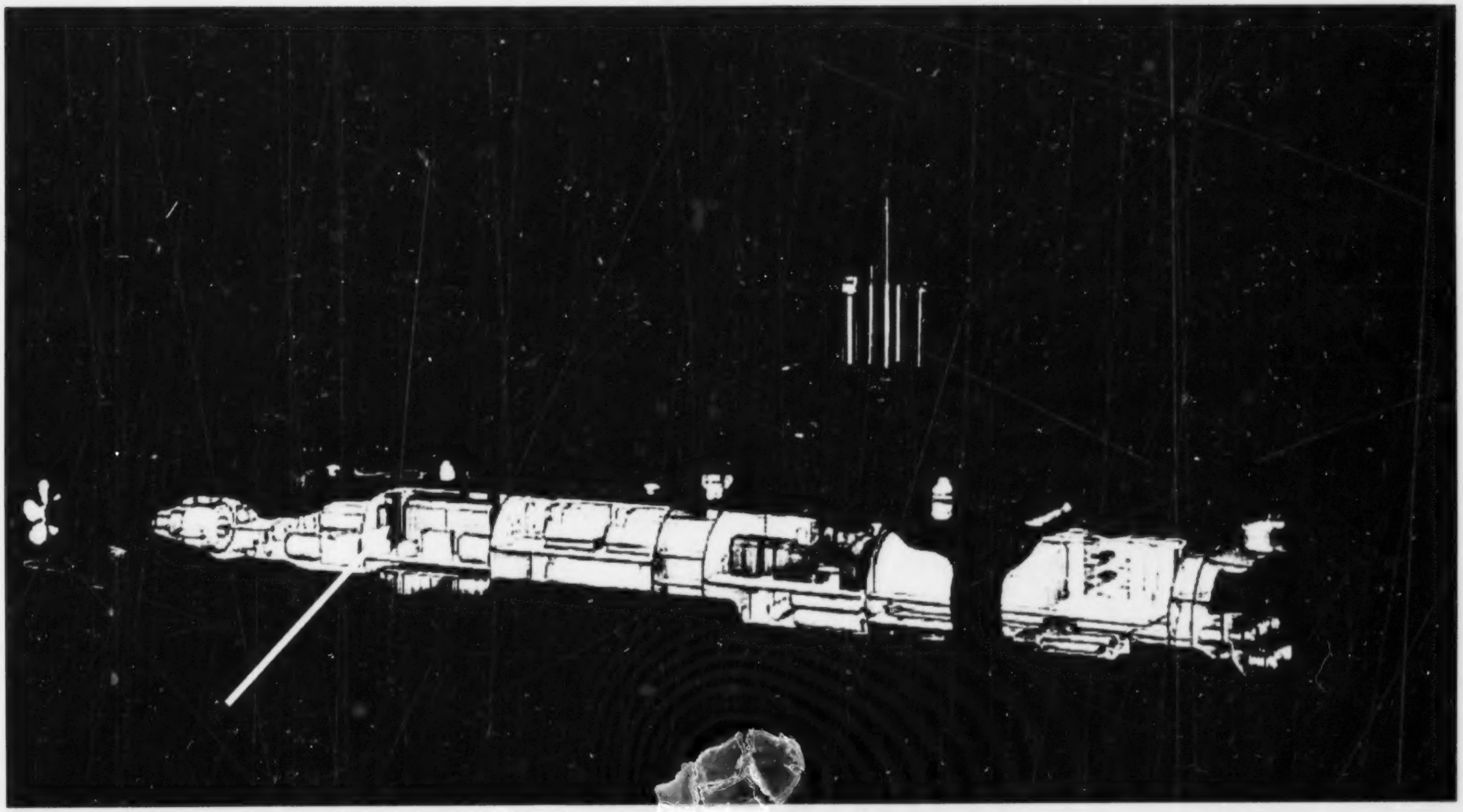
Christina Östberg[1] and Lutz Schauer[2]

[1]Defence Research Establishment, Defence Medicine,
Hårsfjärden, Sweden.
[2]Astrium GmbH, Friedrichshafen, Germany

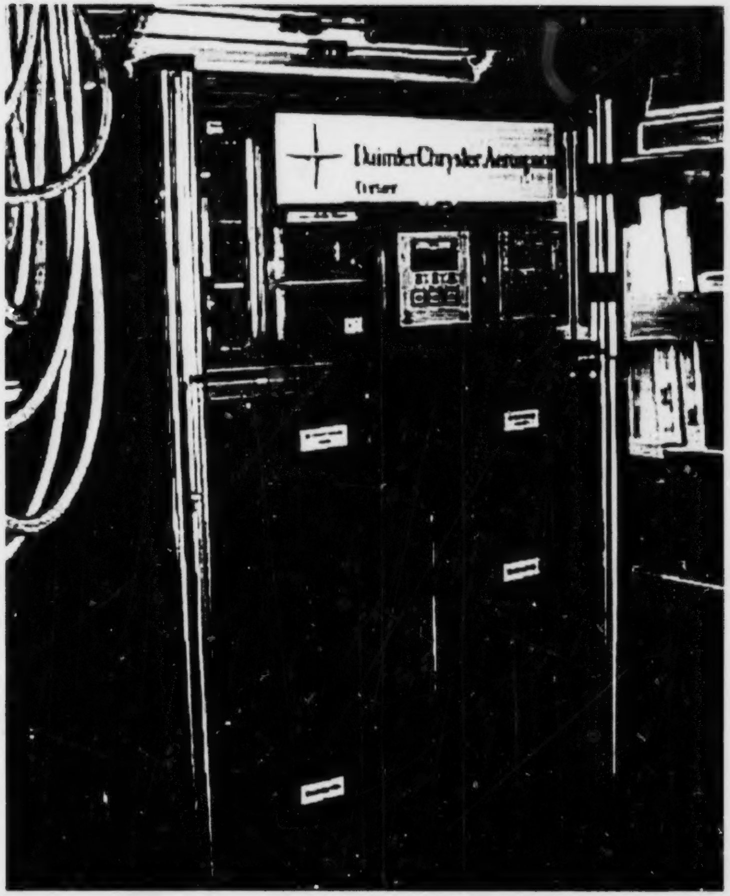
FOA

CO_2 scrubbing system for use in small confined spaces

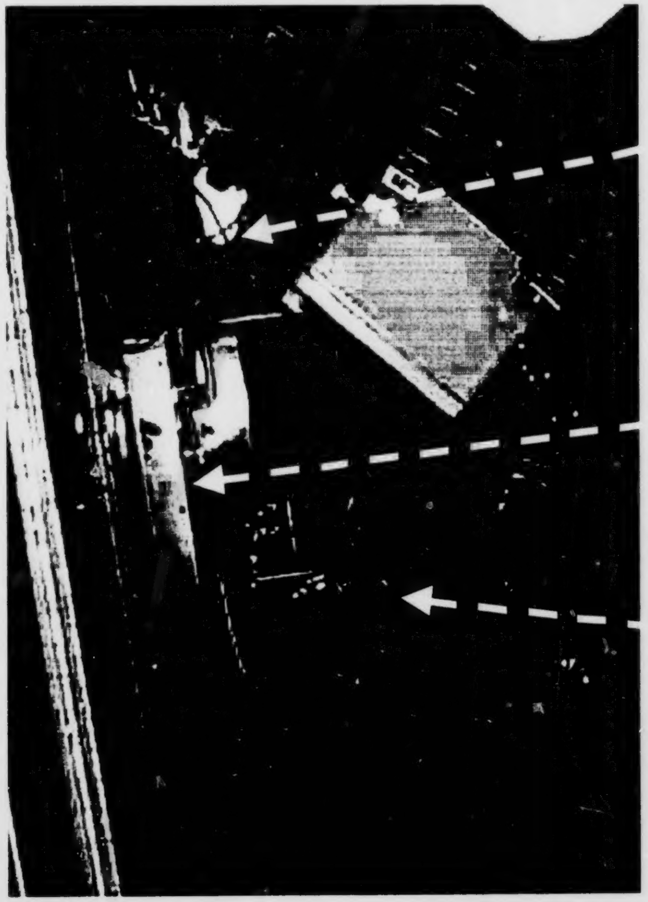
- Simple
- Regenerative
- Low Power Consumption



FOA DEFENCE MEDICINE


DaimlerChrysler Aerospac

FOA DEFENCE MEDICINE



Air Quality Monitor

CO_2 Scrubber

Steam generator

Laboratory tests

- overheating (100- 130 °C)
- smoke generation test (ISO 5659-2)
- smoke gas toxicity

FOA DEFENCE MEDICINE

Test protocol, on board trials

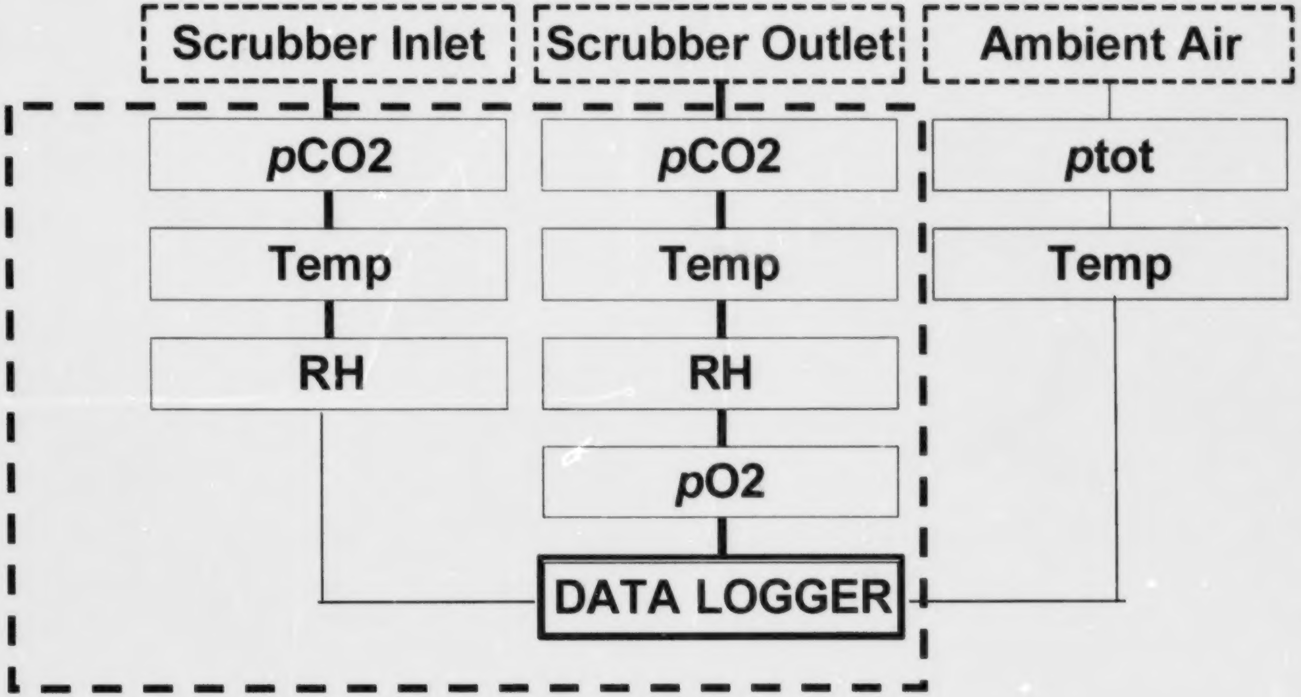
Trials at sea

- 446 h, 15 occasions (1 - 75 h)
- 0 - 0.5 kPa CO_2 (18 h > 0.4 kPa)

Trials at quay

- 66 h
- 0.2, 0.5, and 0.8 kPa CO_2

Air Quality Monitor



Scrubber Inlet
*p*CO2
Temp
RH

Scrubber Outlet
*p*CO2
Temp
RH
*p*O2
DATA LOGGER

Ambient Air
*p*tot
Temp

FOA DEFENCE MEDICINE

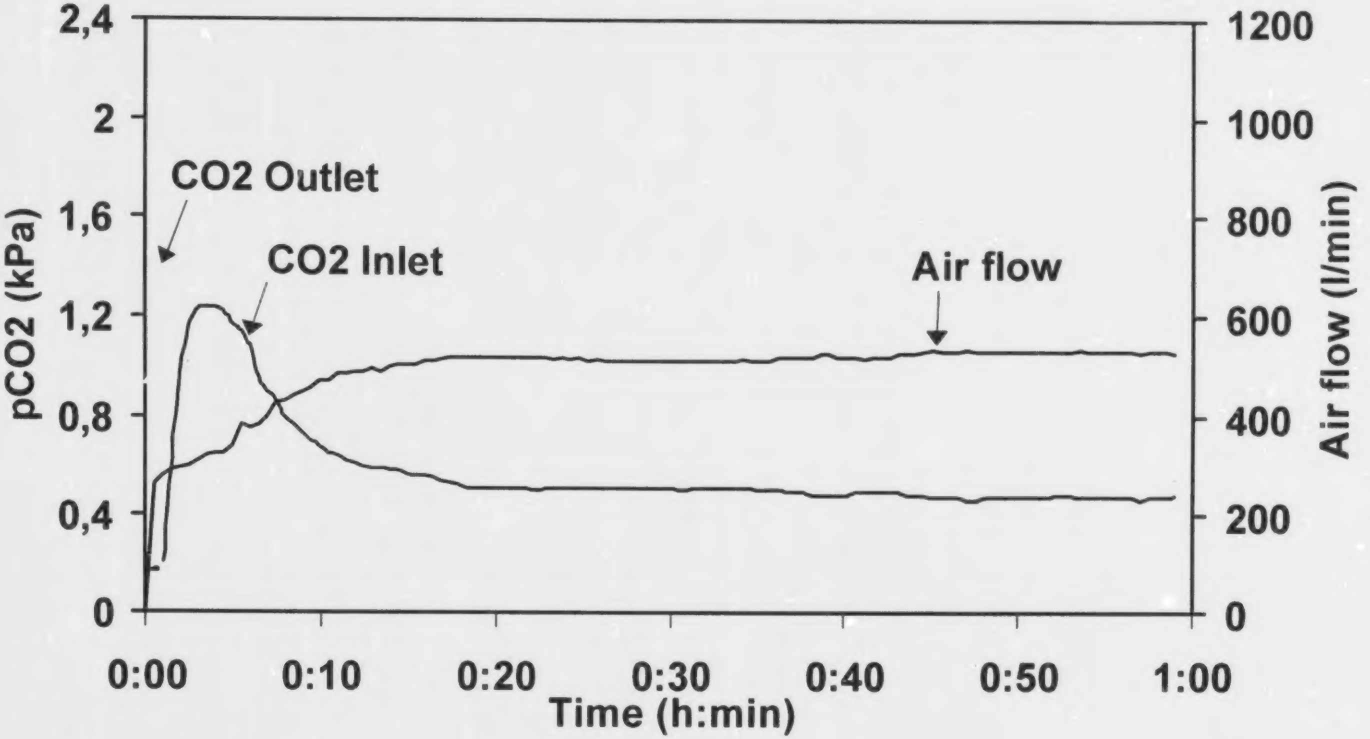
Draeger CMS

- NH_3
- CO
- SO_2
- NO_x
- NO_2

GC/MS

- Benzylamine
- TVOC

Quay trials
(inlet CO_2 0.5 kPa)



FOA DEFENCE MEDICINE

CONCLUSIONS

Nothing has yet been found that would make scrubbers based on solid amine unsuitable for use on board submarines, but the technical problems with the installation and the prototype used made it impossible to make conclusive tests.

However:

- With 0.6 kPa CO_2 in the inlet air the scrubber eliminated 0.54 l CO_2/man and min.
- Benzylamine or other toxic gases have not been found during routine operation.
- At overheating (incomplete combustion) NH_3 may be released.

On board trials with a regenerative carbon dioxide scrubber

Christina Östberg and Lutz Schauer

kicki@sto.foa.se

Development of Action Levels for Toxic Atmospheric Contaminants in a Disabled Submarine

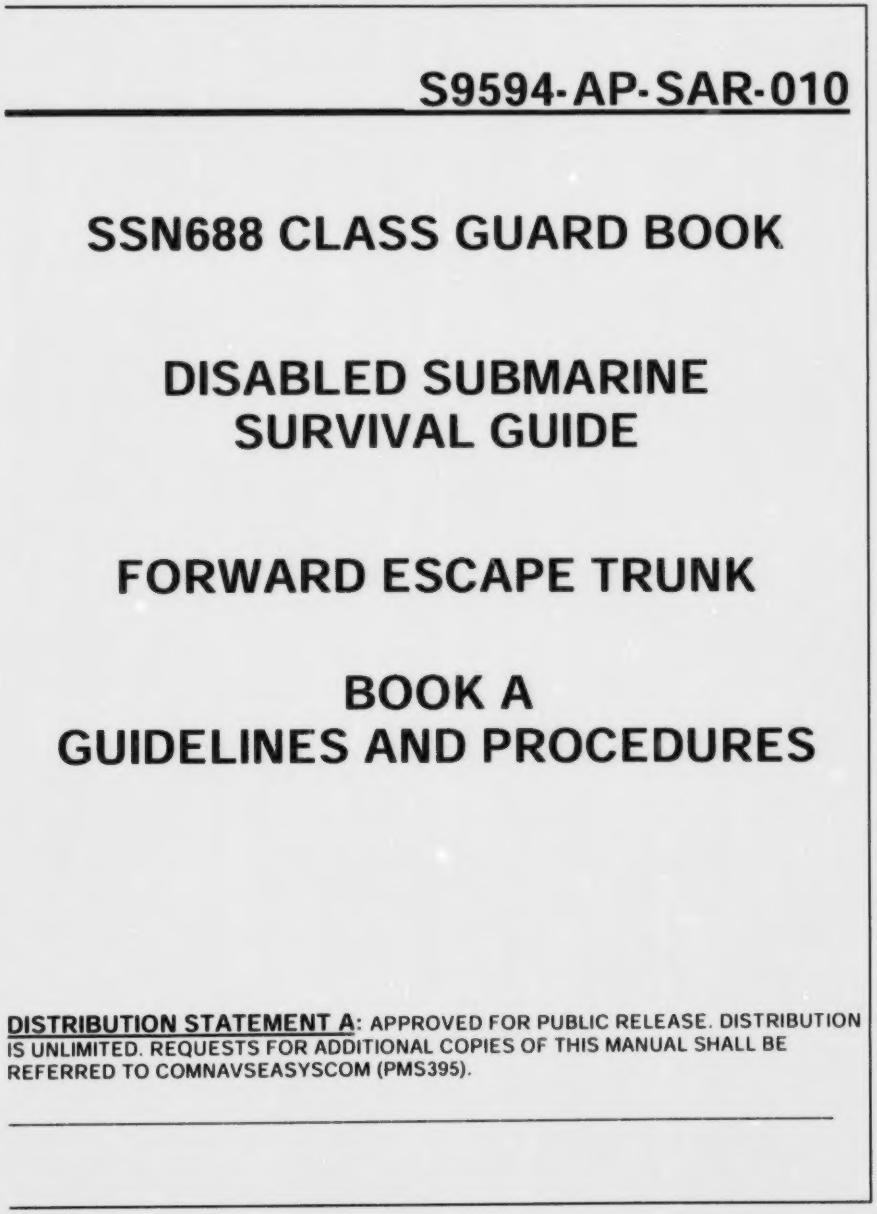
LT C.L. Wilson, MSC, USNR
SurgCDR S. Ryder, RN
CDR W. Horn, MC, USN
Dr. R.L. Carpenter
CDR W.K. Alexander, MSC, USN
CAPT K.R. Still, MSC, USN

Introduction

- Historical:
  - Over 101 non-combatant sinkings
  - 2500 lives lost
  - Most incidents shallower than 300 feet
- Potential Causes of Submarine Disasters:
  - Fire
  - Flooding
    - Hull Failure
    - Fixture Failure
  - Collision
  - Grounding

Submarine Escape

- Depths of 450 - 600 ft
- 6 - 8 Survivors/hr
- Risks
    - Decompression Illness
    - Hypothermia
    - Marine Wildlife



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SSN688 CLASS GUARD BOOK

DISABLED SUBMARINE
SURVIVAL GUIDE

FORWARD ESCAPE TRUNK

BOOK A
GUIDELINES AND PROCEDURES

DISTRIBUTION STATEMENT A: APPROVED FOR PUBLIC RELEASE. DISTRIBUTION IS UNLIMITED. REQUESTS FOR ADDITIONAL COPIES OF THIS MANUAL SHALL BE REFERRED TO COMNAVSEASYSCOM (PMS395).

Survivor Guidance

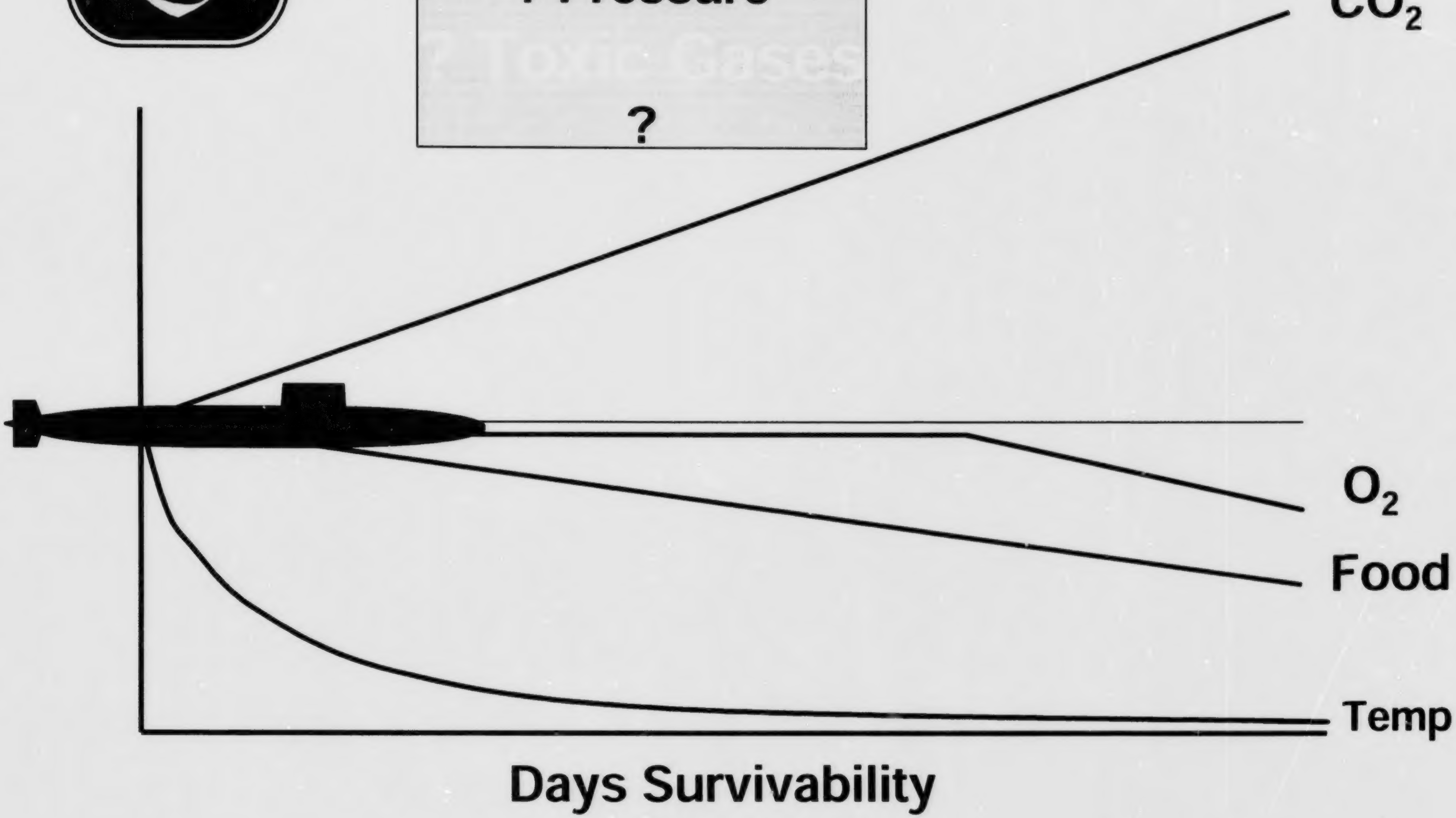
- Survival
- Escape vs. Rescue

Submarine Survival Outline

? Pressure

? Toxic Gases

?



Identification of Combustion Products

- Know composition of hardware components on submarines and can predict major thermal degradation products;
- Major fire gases have been studied extensively individually and in combination
  - CO_2, CO, HCl, NO_x, SO_x, NH_3, Cl_2, H_2S, HCN

Objective

- To assist Naval Submarine Medical Research Laboratory in developing toxic gas action levels for use in risk-based management of survivors of a disabled submarine (DISSUB)

Submarine Escape Action Levels (SEALs)

SEAL 1--Limit below which survivors can remain in the compartment without wearing respiratory protection for a maximum period of 10 days. *If SEAL 1 is exceeded (but SEAL 2 is not) survivors will not wear EABs but will plan to escape within 24 hours. Exceedence of SEAL1 may result in inhibition of ability to escape.*

SEAL 2--At and above this level survivors are required to wear EABs because unprotected exposure to the contaminant for less than 24 hours will result in significant impairment to respiratory and/or CNS function which will impair their ability to conduct an escape. *If SEAL 2 is exceeded, the crew should initiate their escape immediately.*

Submarine Escape Action Levels

Gas Level	EABs?	Action
< SEAL 1	No	Wait
> SEAL 1& < SEAL 2	No	Escape within 24 hours
> SEAL 2	Yes	Escape now

Carbon Monoxide (CO)

- *SEAL 1 = 75 ppm; SEAL 2 = 85 ppm*
- Based on goal of maintaining [COHb] between 8.3 and 12.4%;
  - 50% generally considered lethal (4,6,25)
  - nausea & vomiting produced as low as 15% (incompatible with EABs) (SMACs Vol. 1)
- Early effects on motivation and psychomotor ability are important; however, significant behavioral decrement controversial at <20% COHb (4)
- Important to consider difficult & demanding intellectual effort
- Incapacitation suggested within 30 min of exposure to 1000 ppm (<37% COHb) performing light work (1 study) (6)
- Potential interactive effects with HCN, CO_2 (26)
- Adaptation takes ~16d in humans (SMACs Vol.1)

Hydrogen Chloride (HCl)

- *SEAL 1 = 2.5 ppm; SEAL 2 = 25 ppm*
- Based on immediate irritant effects on mucous membranes observed at >50 ppm (9);
- Tolerable up to 100 ppm (9, 11, 13, 14)
- No systemic effects known (9)
- Exposure for 60 min to 2 to 3 ppm disagreeable in some subjects and significant irritation reported as low as 10 ppm, although probably not immediately threatening to performance
- Other considerations:
  - HCl will likely exist as an aqueous aerosol vs anhydrous vapor under DISSUB conditions, suggesting a potential dermal exposure

Hydrogen Cyanide (HCN)

- *SEAL 1 = 1 ppm; SEAL 2 = 4.5 ppm*
- Based on:
  - PEL of 4.5 ppm, 7-d SMAC of 1 ppm, IDLH of 50 ppm (30,29)
  - CNS as target organ
- Good dose-response inhalation data for human and animal studies is lacking (most studies are at high doses)
- Demonstrated interaction between CO and HCN, suggesting incapacitation by HCN may result in increased exposure to CO (25,26);

Nitrogen Oxides (NO_2)

- *SEAL 1 = 0.5 ppm; SEAL 2 = 1 ppm*
- Based on:
  - Ocular and nasal irritation at 10 to 20 ppm (40);
  - Induction of bronchitis or pneumonia at 25 to 75 ppm (38)
  - 300 to 500 ppm may be fatal (38)
  - Immunotox effects may be important in the event of an escape (35,40)
- Draeger tube available for NO_2 only
- Current ACGIH STEL of 5 ppm

Sulfur Dioxide (SO_2)

- *SEAL 1 = 3 ppm; SEAL 2 = 6 ppm*
- Based on:
  - bronchoconstriction (37)
  - increase in airway resistance at >3 ppm for 120 h (45,46)
  - irritant gas in combination with asphyxiants and particulate
- Aerosol formation influenced by particulate and humidity (41,42)

Hydrogen Sulfide (H_2S)

- *SEAL 1 = 10 ppm; SEAL 2 = 20 ppm*
- Based on:
  - possible interaction with HCN (55)
  - pulmonary edema reported in prolonged exposures as low as 50 ppm (60)
  - Ocular toxicity at 5 to 30 ppm (48-52)
- Changes in vision could compromise efficiency of task completion

Chlorine (Cl_2) (g)

- *SEAL 1 = 2 ppm; SEAL 2 = 5 ppm*
- Based on:
  - COT guidance of 3 ppm ceiling for 60 minutes for submarine crews (1973 Report)
  - significant respiratory irritation in humans at 5 ppm (9)
  - Eye irritation threshold at 7.7 ppm (9)
  - 40-60 ppm for <1 h lethal (9)

Ammonia (NH_3)

- *SEAL 1 = 25 ppm; SEAL 2 = 75 ppm*
- Based on:
  - Concentrations of approx. 25 ppm result in some irritation (64)
  - reports of severe pulmonary irritation at 100 ppm (63);
  - Previous Navy reports suggest 25 ppm as maximum limit for continuous exposure (65)
- Concerned with combined exposure to irritant gases

Cumulative Effect Index (CEI)

- Describes interaction between gases
- $M_{HCl}/SEAL_{HCl} + M_{HCN}/SEAL_{HCN} + \ldots$for all gases except CO <1
- Assumes additivity

Major Unanswered Questions

- Health effects of exposure to an atmosphere that contains one or all of these gases at levels of concern, especially when atmosphere is **high relative humidity, hyperbaric, and low temperature**.
- Specifically, what is the interaction between these chemicals under the specified conditions?

Other Considerations

- Lack of reliable and accurate portable detection technologies;
- Potential variability in compartment pressure
- Multiple pulmonary injuries from fire and smoke inhalation may reduce chances of survival during free ascent in the event of an escape

Other Considerations, cont'd

- Cumulative Effect Index (CEI) assumes only additivity:
  - CO+HCN: synergism, additivity, or no effect?(26)
  - CO+CO_2: antagonism, no effect, or additivity?(26)
  - CO+SO_2: enhanced activity of SO_2 (2)
  - CO+ΔT: enhanced by temp. above or below ambient (2)
  - CO+HCl: additive (Hartzell, 1990)
  - CO_2 + other fire gases: synergism (Levin, 1996)
  - HCN+NO_x: antagonism (Levin, 1996)
  - HCN+H_2S: antagonism (55)
- Low O_2 appears to enhance toxicity of many fire gases in at least one model (Levin, 1996)
- Role of particles

Recommended SEALs

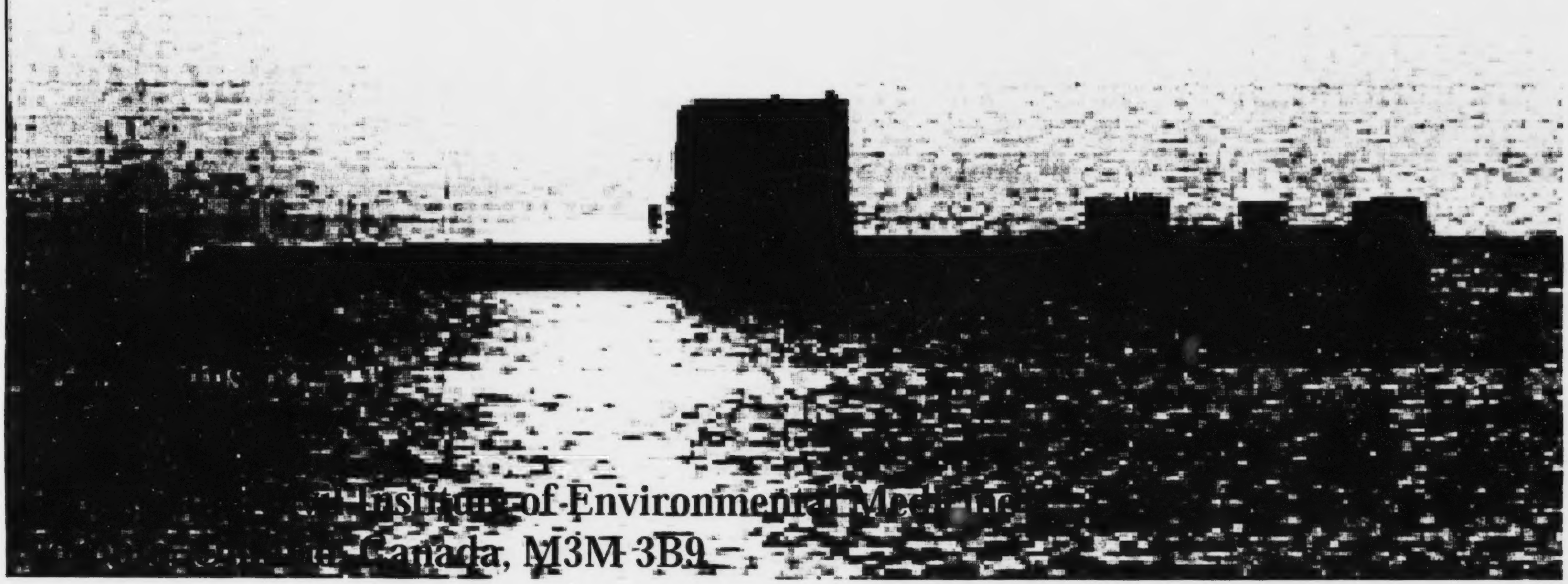
GAS	SEAL 1[1]	SEAL 2	TLV	SMAC[3]	ACM[5]
Carbon monoxide	**75**	**85**	25	55/20/10	55/20
Hydrogen chloride	**2.5**	**25**	C[2] 5	NA[4]	5/2
Hydrogen cyanide	**1**	**4.5**	C 4.7	NA	none
Nitrogen oxides	**0.5**	**1**	3	NA	3/1
Sulfur dioxide	**3**	**6**	2	NA	5/2
Hydrogen sulfide	**10**	**20**	10	NA	none
Chlorine	**2**	**5**	0.5	NA	1/0.5
Ammonia	**25**	**75**	25	30/20/10	30/20

[1] —values for SEALs 1 and 2, TLVs, SMACs, and ACMs are listed in ppm;
[2] —C = TLVceiling;
[3] —SMAC listed as 1h/24h/7d limits;
[4] —NA = data not currently available;
[5] —ACM listed as 1h/24h limits.

An Air Quality Assessment Onboard an Oberon Class Submarine:

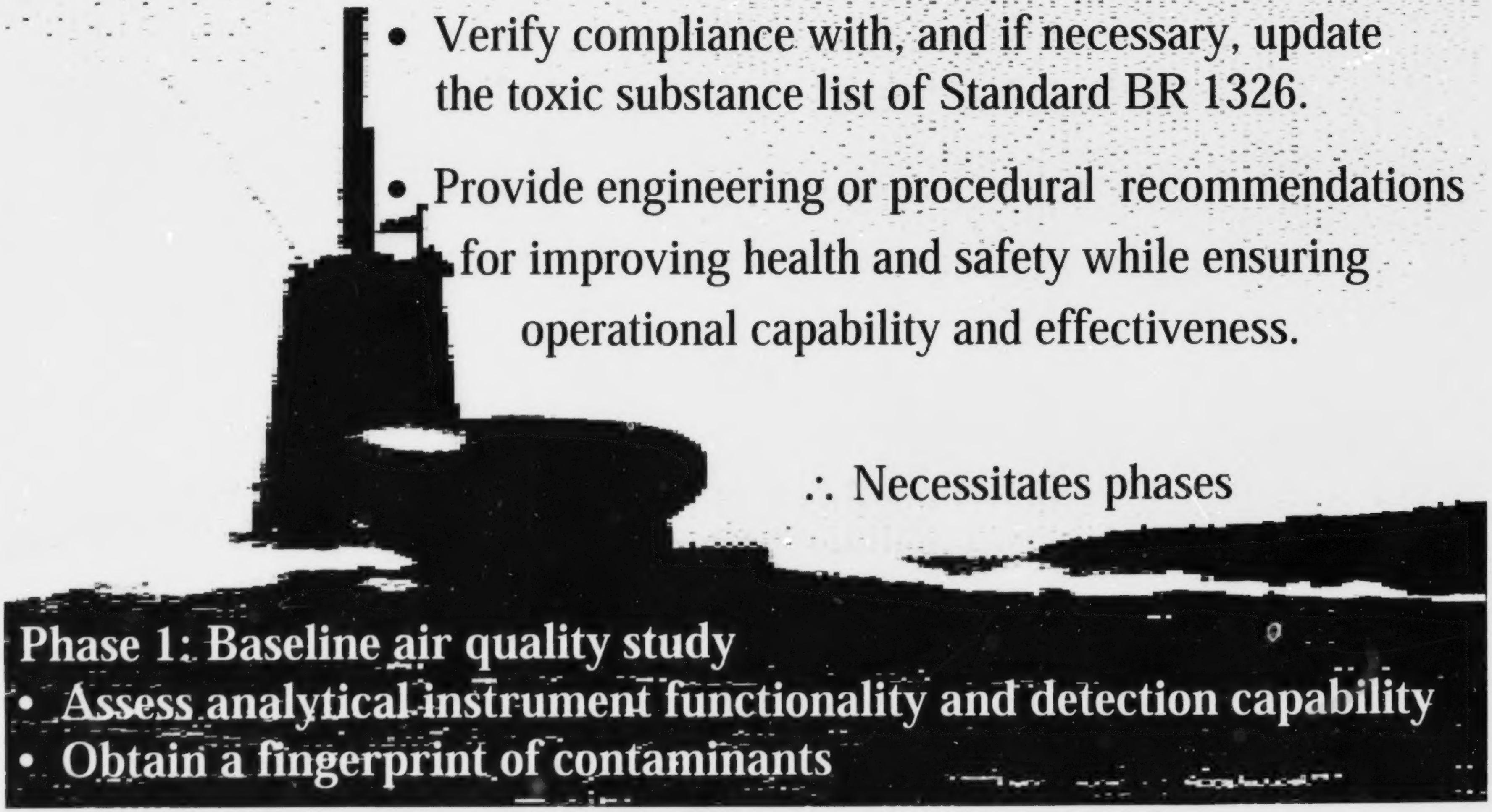
HMCS Okanagan

Canadian Submarine Habitability
and Progress for the Future



[illegible] Institute of Environmental Medicine
[illegible] Canada, M3M 3B9

Tasking Objectives



- Identify and quantify contaminants found under all operational scenarios.
- Verify compliance with, and if necessary, update the toxic substance list of Standard BR 1326.
- Provide engineering or procedural recommendations for improving health and safety while ensuring operational capability and effectiveness.

∴ Necessitates phases

Phase 1: Baseline air quality study

- Assess analytical instrument functionality and detection capability
- Obtain a fingerprint of contaminants

[illegible]

1. Assist operational managers in:

   a. Maintaining acceptable atmospheric quality onboard submarines.
   b. Developing and maintaining a reliable atmosphere- monitoring policy.
   c. Establishing a submarine smoking policy.
   d. Developing smoke clearance procedures.

2. Provide the medical community with an atmospheric snapshot of the environment.

3. Provide recommendations for reliable and accurate atmospheric monitoring equipment.

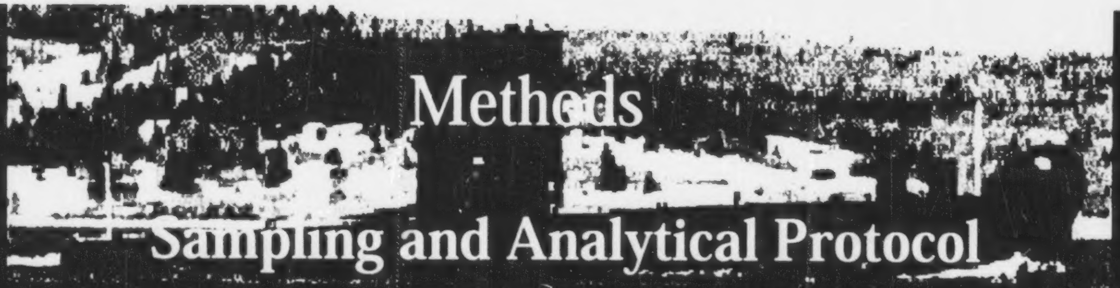
Methods

Test Protocol

Monitor true environmental conditions - under patrol conditions
- maintaining routine operational procedures and standard policies
  - including air purification and monitoring of contaminants
    Oxygen, Carbon Dioxide and Carbon Monoxide

Continuous monitoring enabled a reasonable assessment of:
- air purification capabilities
- routine housekeeping procedures (cleaning and cooking)
- lifestyle effects (smoking)

Monitoring during the two-hour snort period assessed
- effectiveness of snorting, and the resulting air exchange
- effects of battery charging



Methods

Sampling and Analytical Protocol

Compounds selected for monitoring:

- potentially life threatening or
- carry a risk of producing long-term chronic symptoms, and
- documented in Standard permitting assessment of compliance.

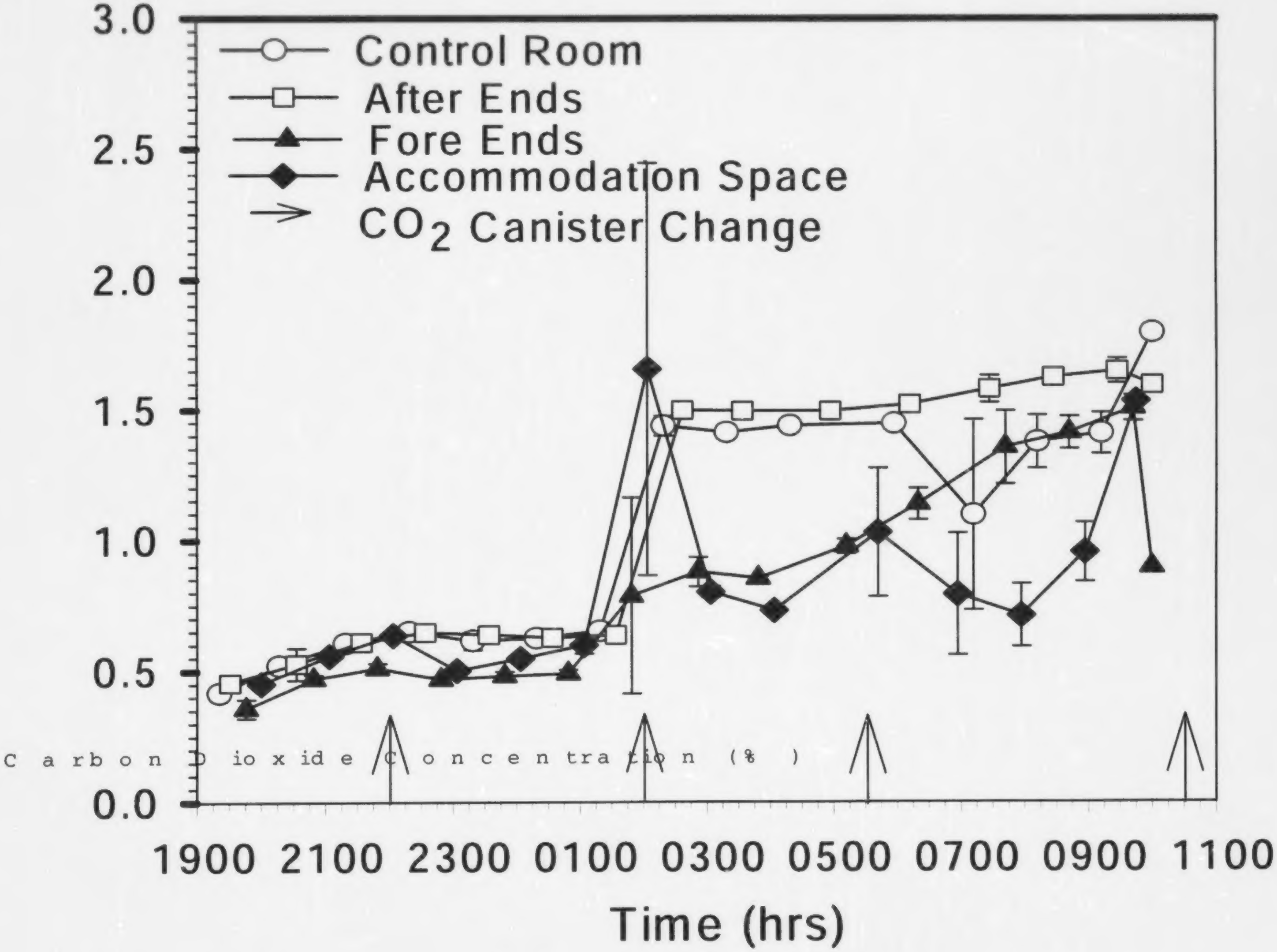
Air constituents or contaminants monitored:

Carbon Monoxide; Carbon Dioxide; Oxygen; airborne respirable particulates; Arsine; Stibine; and, Diesel organic compounds; Hydrogen; Ammonia; Ozone; and, Nitrous Fumes

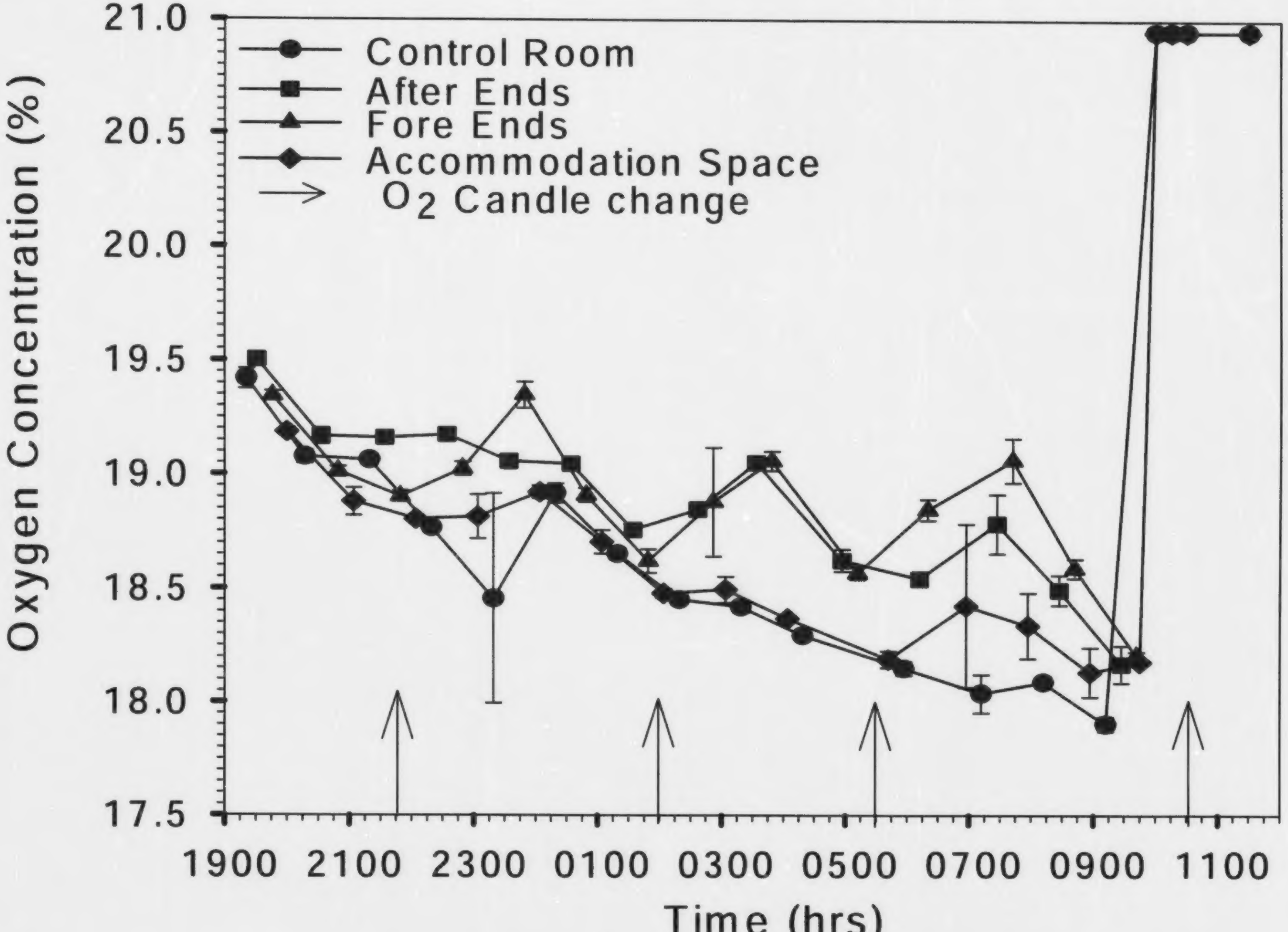
Monitored using:

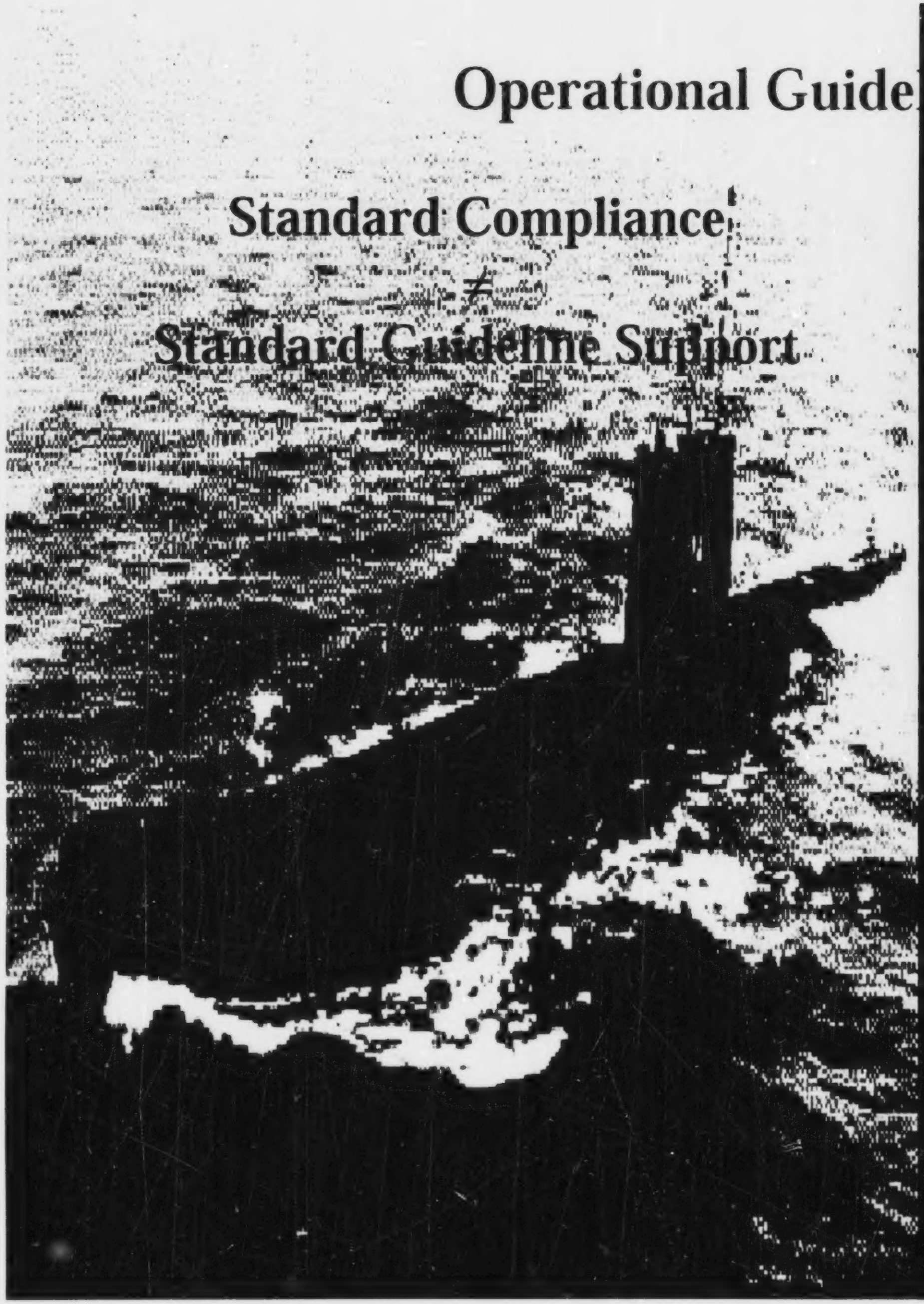
- real-time instrumentation, colorimetric tubes, and grab samples.
- biological uptake of CO was measured by Carboxyhemoglobin.

Variation in Carbon Dioxide Concentration and Effects of Scrubbing



Variation in Oxygen Concentration and the Effects of Air Purification





Operational Guide

Standard Compliance

≠

Standard Guideline Support

Interpretation & Application of Standard

=

Composition of the Atmosphere

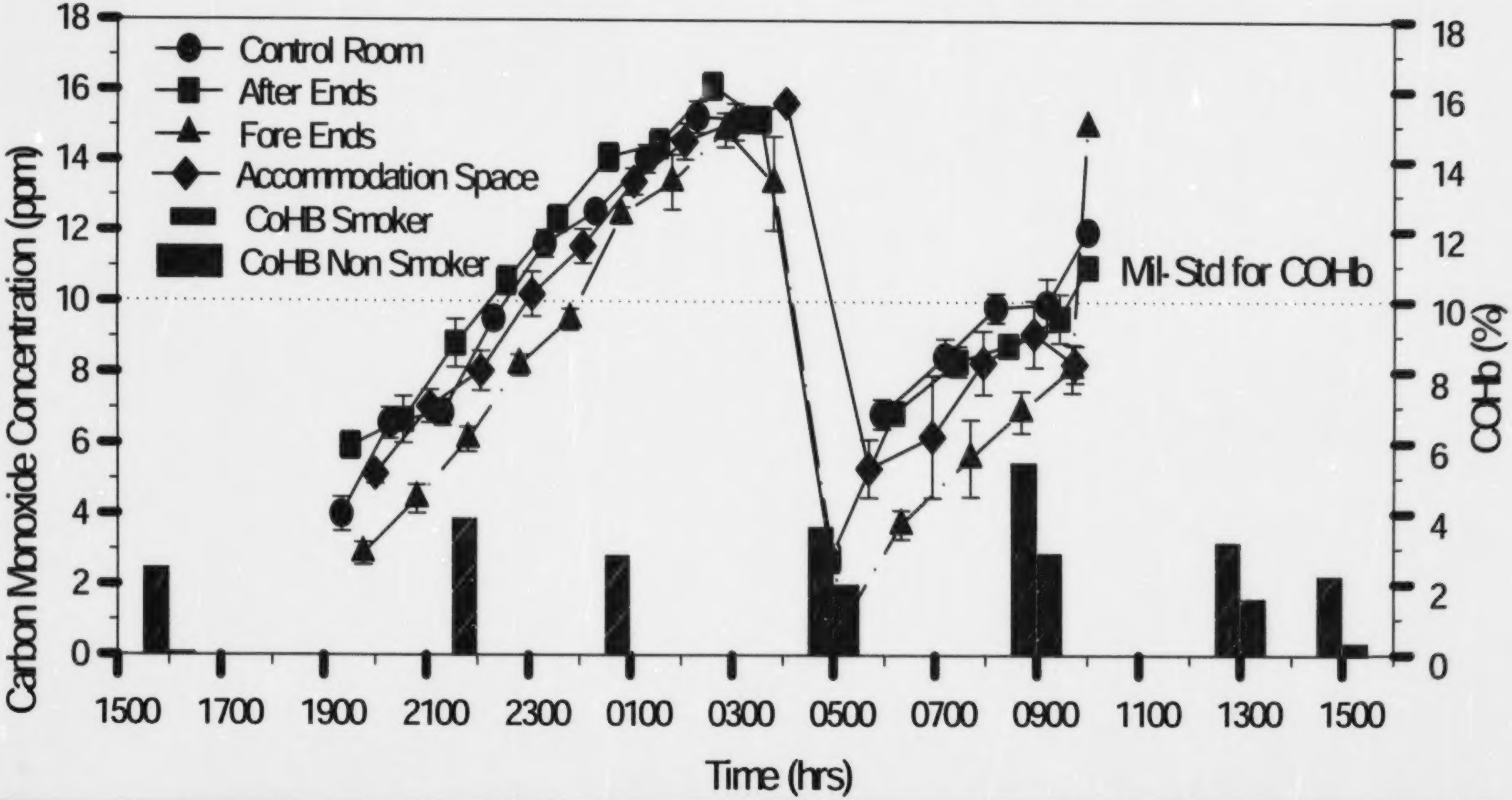
No CO_2 canister or O_2 candle schedules
No Formulae to predict replacement

Weak Link:

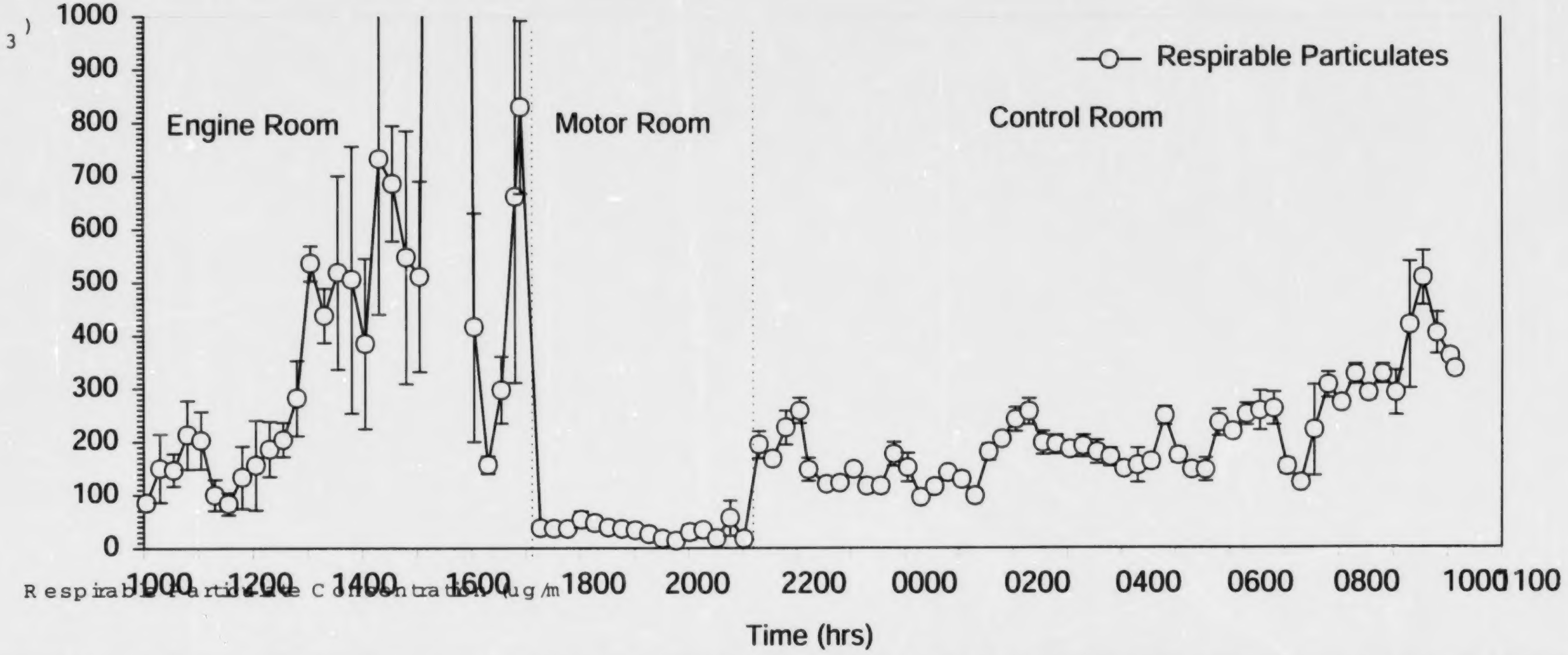
Inaccurate and Unreliable Measurement Methods

Risk: Miscalculation

Variations in Carbon Monoxide and Carboxyhemoglobin Concentrations



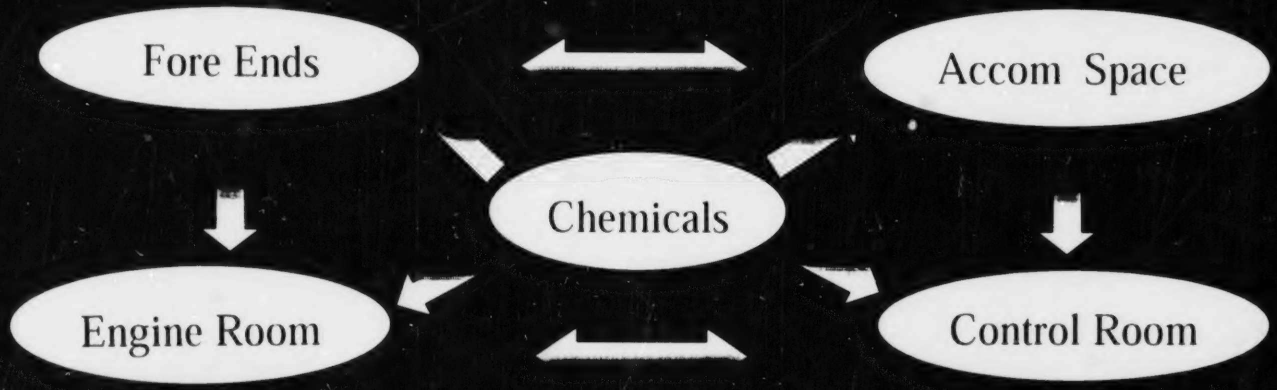
Consecutively Measured Total Inhalable Particulate Concentration



Organic Contaminants

Presence: Chemicals brought into the submarine
Chemicals inherent to construction

∴ Chemicals can off-gas and accumulate

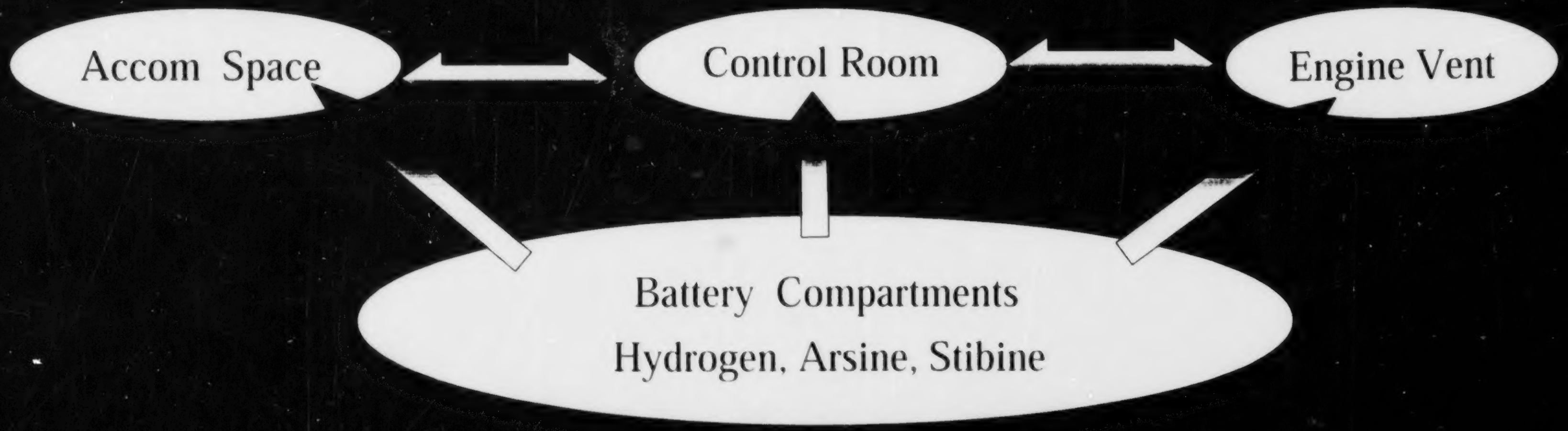

Fore Ends
Accom Space
Chemicals
Engine Room
Control Room

Diesel Effluent : Benzene, Toluene, Ethylbenzene, Xylene
Petroleum Products used in fuels, solvents and degreasers
} Well within Specifications

Concern: At best irritants, at worst carcinogenic

Measurement Essential

Effects of Battery Charging



Accom Space

Control Room

Engine Vent

Battery Compartments

Hydrogen, Arsine, Stibine

Minor Contributing Contaminants

Ammonia: presence from sanitary tanks

Ozone: presence from electrical instrumentation

Nitrous gas (NO_x, NO, NO_2): presence from exhaust gases

All contaminants well within specifications

Future Movement

NATO
Collaboration

Submarine Habitability Research

- CO_2 canister schedule
- O_2 candle schedule
- Review and update exposure limits
- Reevaluate standard

Improved Operations

Enhanced
Health and Safety

Submarine Air Quality Management

- Atmosphere policy and procedures
- Monitoring instrumentation
- Engineering controls
- Material toxicity guide

“ Make the boat and the men safe”

Genomic Analysis of Buccal Epithelium and Peripheral Leukocyte Samples from Air Force Jet Fuel Workers: Identification of Biomarkers of Exposure and Implications for Study of Diesel Submarine Crews

C.L. Wilson, W.H. Hanneman, M.Y.V. Bekkedal, and J. Rossi III

Naval Health Research Center Detachment (Toxicology)
Dept of Environmental Health, Colorado State University

Introduction

- Kerosene-type jet fuels are complex & variable mixtures of hydrocarbons
- Single largest exposure in the DoD (5 billion gallons annually)
- No occupational exposure limit (OEL) has been set in the U.S.
- Data collection for a human health risk assessment of acute occupational exposure to JP-8 is currently underway

Acute Exposure to JP-8 Jet Fuel

- Short-term prospective cohort study of Air Force personnel from seven bases
- “Exposed” group includes personnel who routinely perform maintenance activities requiring entry into the fuel tank and must have at least 9 months of such duty
- “Nonexposed” group includes AF personnel who are not routinely exposed to solvents or fuels and are stationed on the same base as the Exposed group

Acute Exposure to JP-8 Jet Fuel: Study Parameters

- Industrial Hygiene Measures:
  - Personal air sampling
  - Grab sampling
  - Constituent analysis of raw jet fuel from each base
- Performance Health Measures:
  - Computer-based neurobehavioral tests to measure motivation, response speed, memory, etc.

Acute Exposure to JP-8: Study Parameters, cont'd

- Performance Health Measures, cont'd:
  - Postural sway
  - Risk factor and medical records reviews
- Biological Measures
  - Internal temperature monitoring
  - blood GST expression and activity
  - GST genotyping
  - AH blood and urinary metabolite analysis
  - Breath & skin exposure sampling
  - Gene expression analysis from blood and buccal (cheek) swabs

Application of Approach to Study of other Complex Hydrocarbon Mixtures

- Diesel, gasoline, etc. exposures are prevalent in other occupations
- Diesel aerosol and vapor generation in diesel electric submarines may introduce a substantial exposure to sailors
- Problems with the AF study if applied to studies of smaller environments and living spaces
  - Large logistical footprint (20-25 people, space and electrical needs require housing in a small building)

Significance/Background of Gene Expression*

- what is a transcriptional signature?
- why are we interested and what does the information tell us about biology

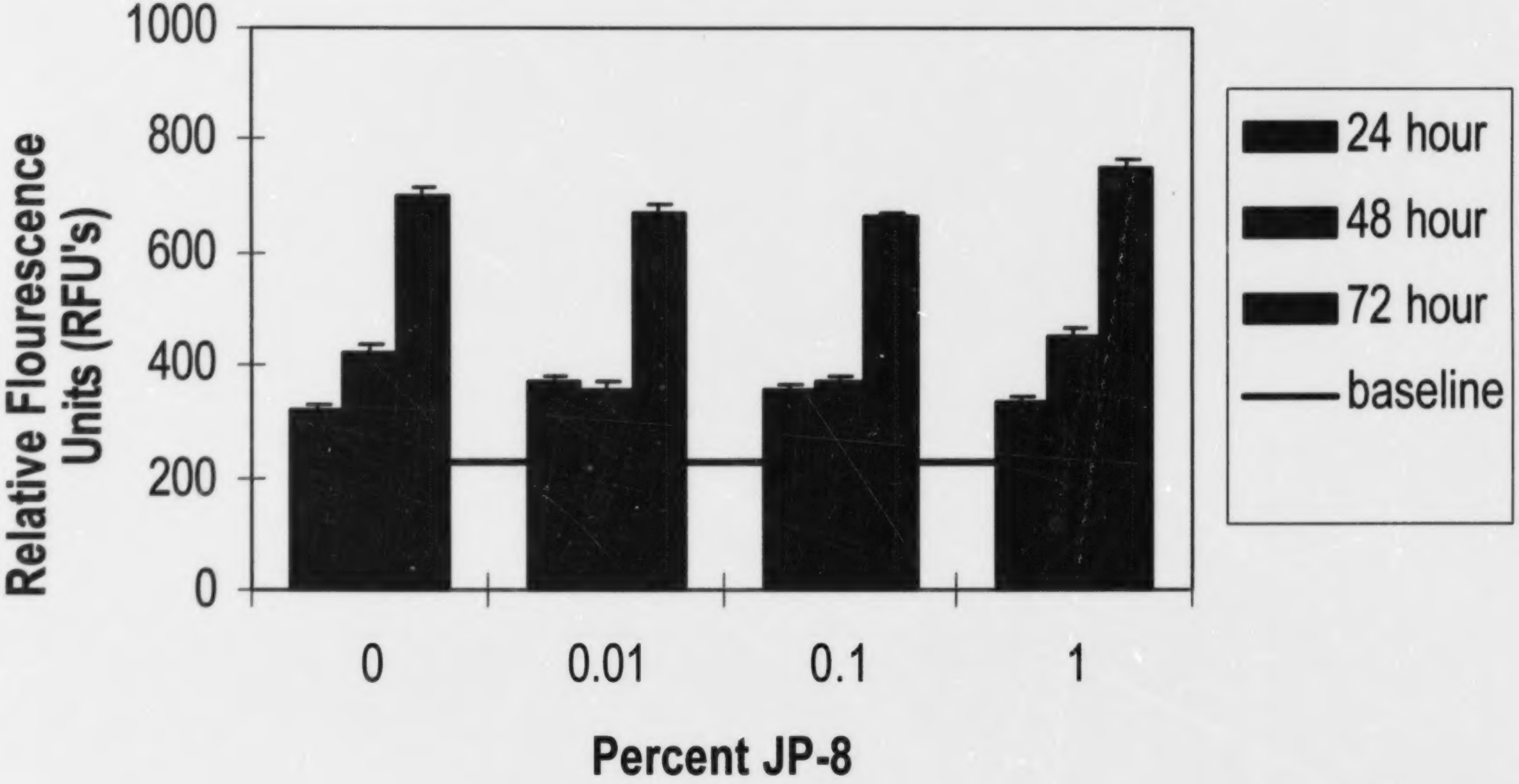
Use of Gene Expression Profiling in Toxicology*

- Gene expression profiling becoming more common
- Transcriptional signature of toxicants to date

Objectives

- To develop a transcriptional signature for human exposure to hydrocarbon fuels
- To correlate transcriptional (in-vitro and in vivo) with behavioral signatures
- To predict xenobiotic-induced human performance changes using gene expression analysis from a non-invasive sampling technique

Cytotoxicity of Human Neuroblastoma Cell Line (SY5Y) to JP-8



Complementary DNA Microarray

Isolate Total RNA

↓

Synthesize and Label cDNA

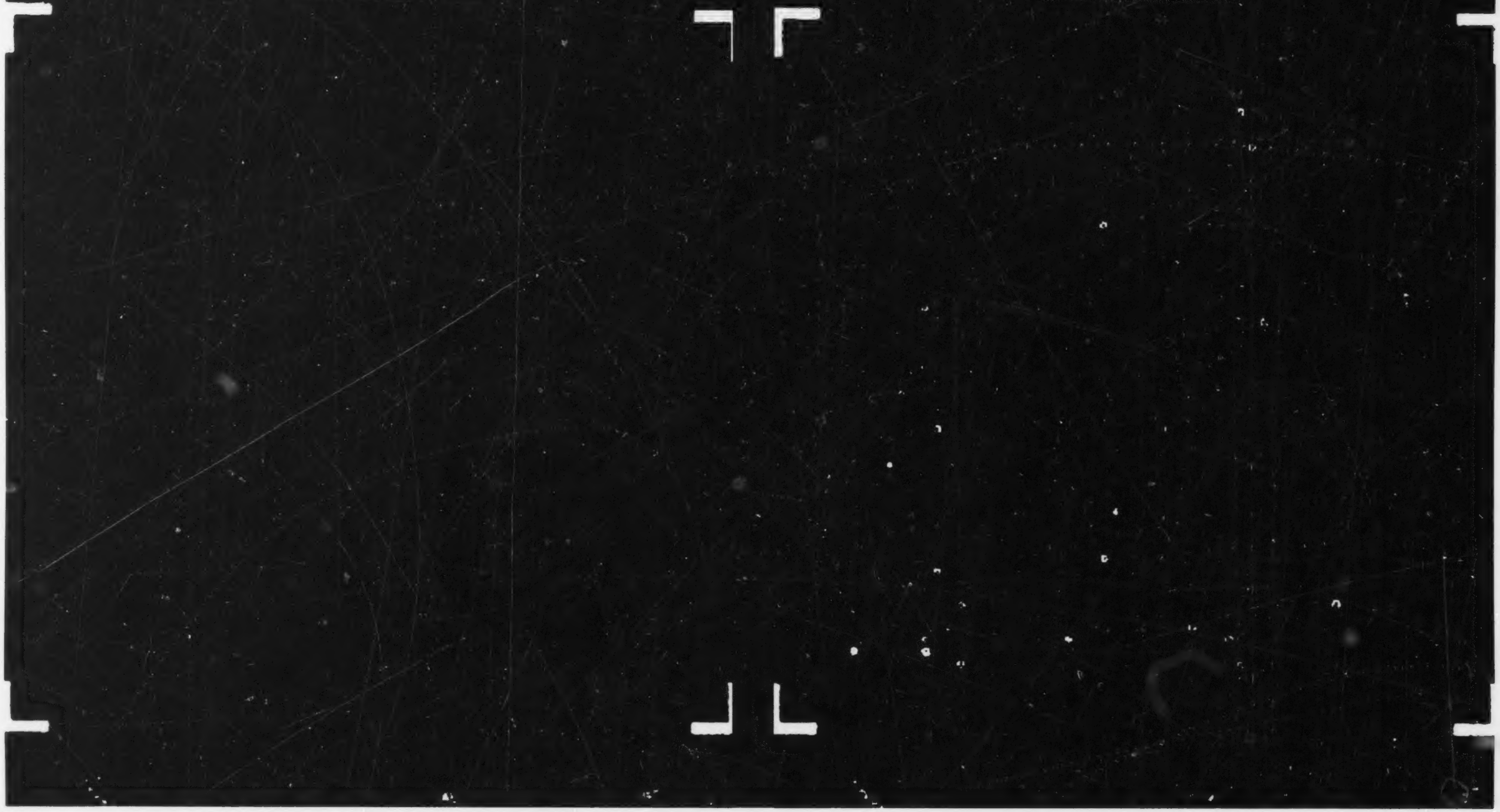
↓

Microarray Hybridization

↓

Scanning and Analysis

Gene Chip Microarray



Control

Treatment

Results of the Gene Expression Assay

- SY5Y cell line treated with JP-8
    - 726 genes under expressed
    - 611 genes over expressed
- Exposed Subject (JP-8)
    - 856 genes under expressed
    - 725 genes over expressed
- Similarities between the two groups
    - 643 genes under expressed
    - 210 genes over expressed

Cluster Analysis of Differentially Expressed Genes

Utilized “focused” analysis to
determine induced/repressed genes

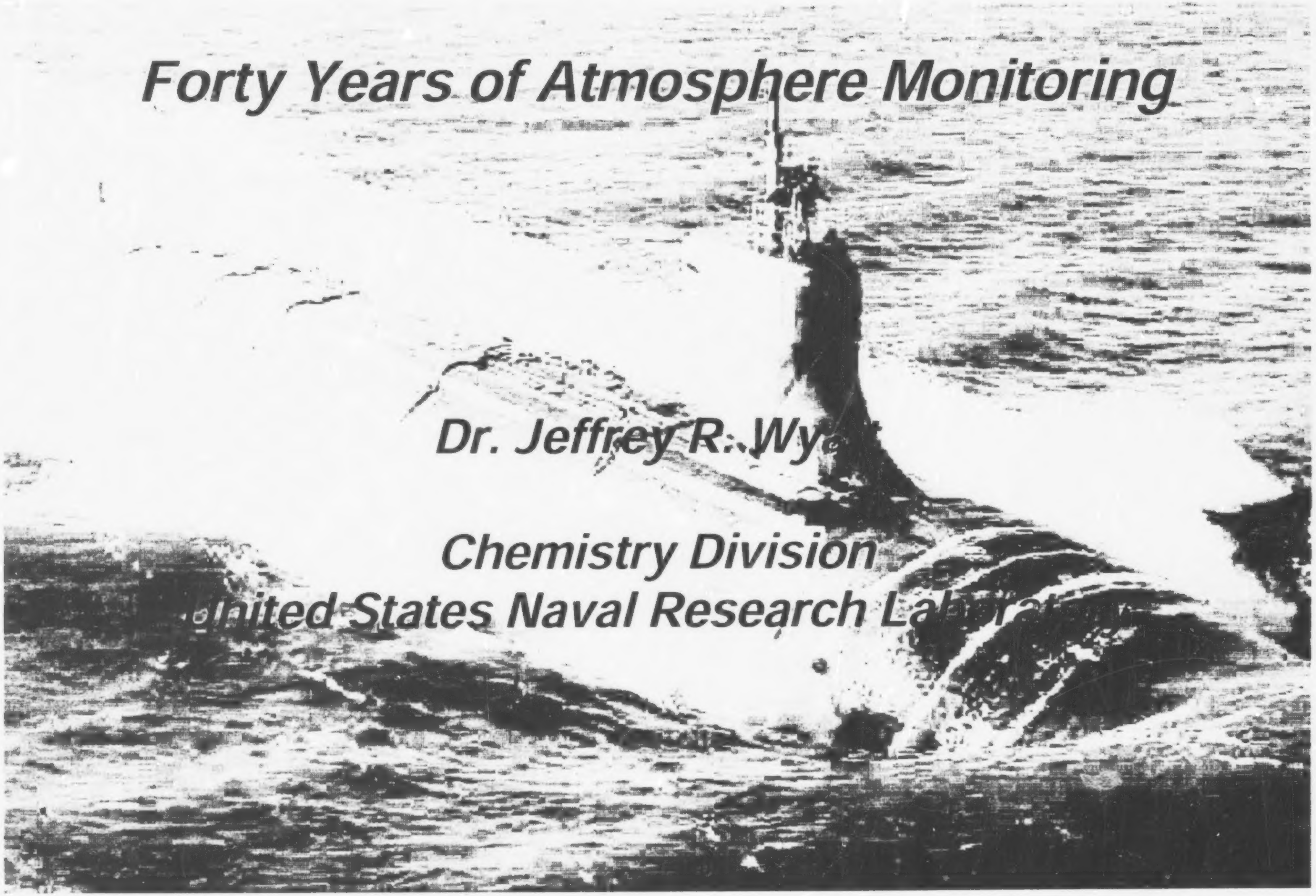
Gene Name	Blood	Buccal
Brain acyl-CoA Hydrolase	3.0	3.0
Brain specific ranodine receptor	4.4	23.1
Neuron specific enolase	6.0	2.55
NF-Kappa B	4.5	2.79
NMDA-receptor modulatory subunit	9.51	12.12
Serotonin 5-HT2 receptor	7.65	17.73
RAD 51d	-8.80	-5.22

Correlation with Neurobehavioral Endpoints (Eye blink)

- Ultimately allows rapid prediction of performance based on changes in gene expression

Application to Diesel Submarine Atmospheres

- Correlation with neurobehavioral endpoints will allow use of transcriptional signature profiling in almost any environment of solvent or fuel exposure
- Logistical footprint is very small
  - One person (vs. 20-25) may collect samples using equipment and supplies that fit in a shoe box
  - No unusual electrical, space, or storage requirements
- Analysis could be performed with data available rapidly (within 1 day of sample collection)



Forty Years of Atmosphere Monitoring

Dr. Jeffrey R. Wyatt

Chemistry Division
United States Naval Research Laboratory

Fleet Concern about Atmosphere Analyzer Reliability

"POLLACK will have a MK IV Atmosphere Analyzer installed. This equipment has been received at New York Shipbuilding Corporation and will be installed in an immediate future. I am concerned with apparent inadequacies and unreliability of this equipment so vital to the proper atmosphere control of a submerged submarine."

H. E. Lyon, Prospective Commander USS POLLACK SSN 603,
letter to the Chief of the Bureau of Ships, 17 July 1962

SUBMARINE ATMOSPHERE ANALYZERS
HISTORICAL SUMMARY

Unit	Technology	Comments	Time Deployed
Mark I	IR	Prototype only	1954
Mark II	IR	No Freon Detection	1955
Mark III	IR	First Production System	1958
Mark IV	IR	Improved Mark-III	1961
Mark V	GC	Unreliable	1968
Mark VI	IR	Like Mark-IV, but less reliable	1970
CAMS-I	MS IR for CO	Full Mil Spec	1975
CAMS-II	MS IR for CO	State of the art, computer controlled	1992

Note: Mark I to IV and Mark VI used paramag. for O_2 and thermoconductivity for H_2

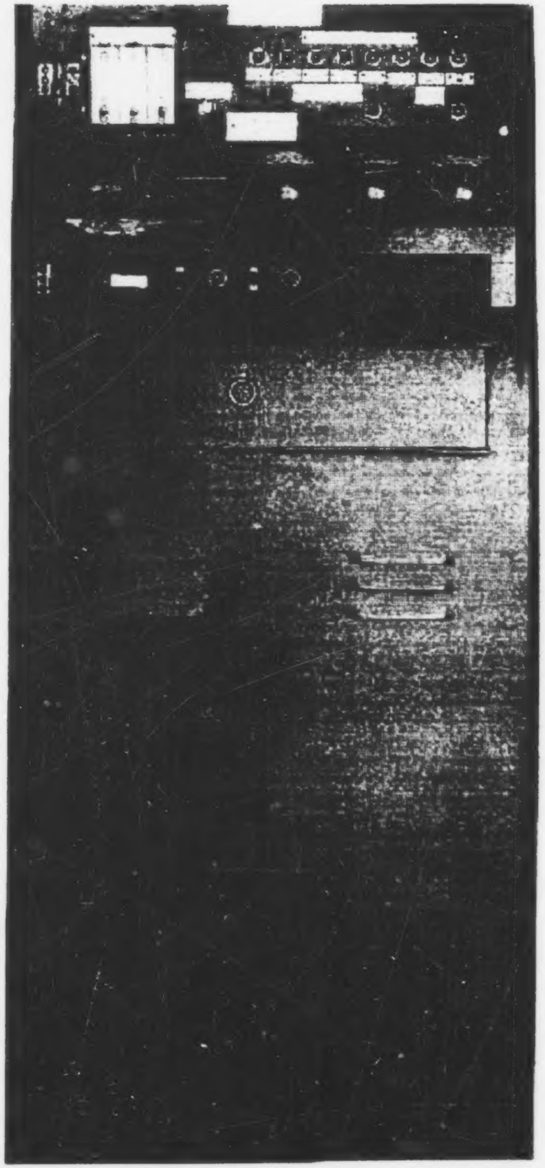
Mark- I Analyzer

Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Hydrocarbons?

????

Mark- II Analyzer

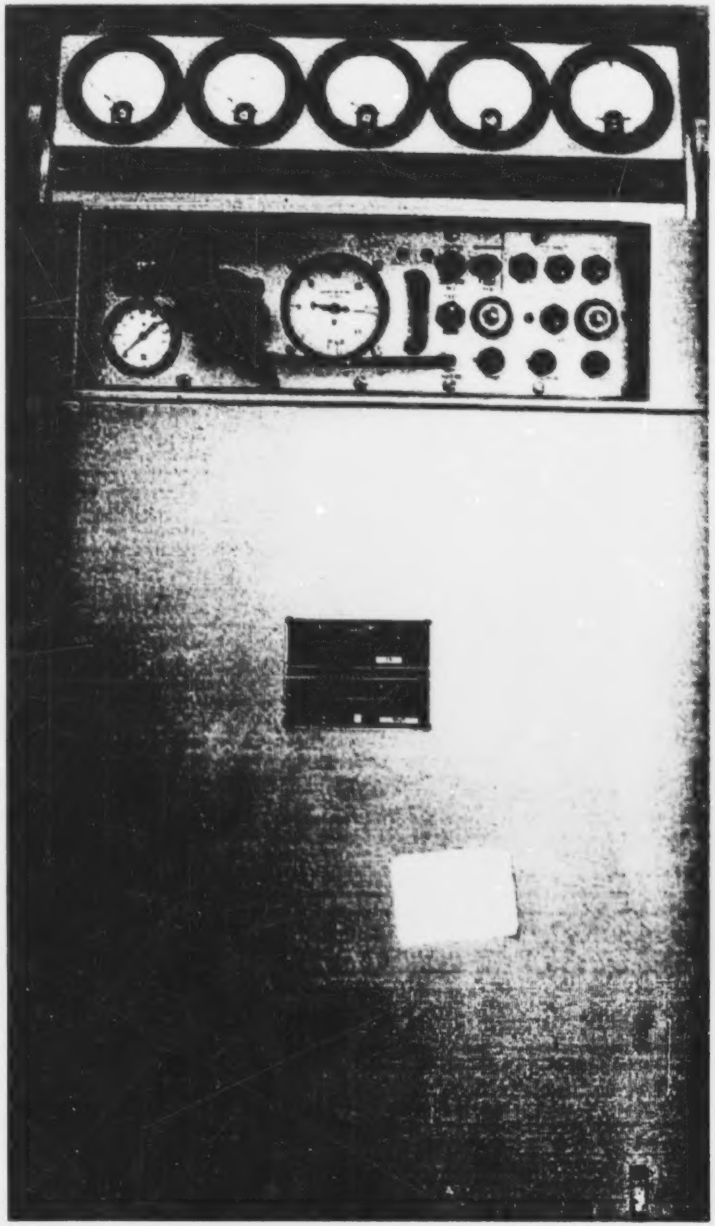


Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Hydrocarbons

- *No Freons*

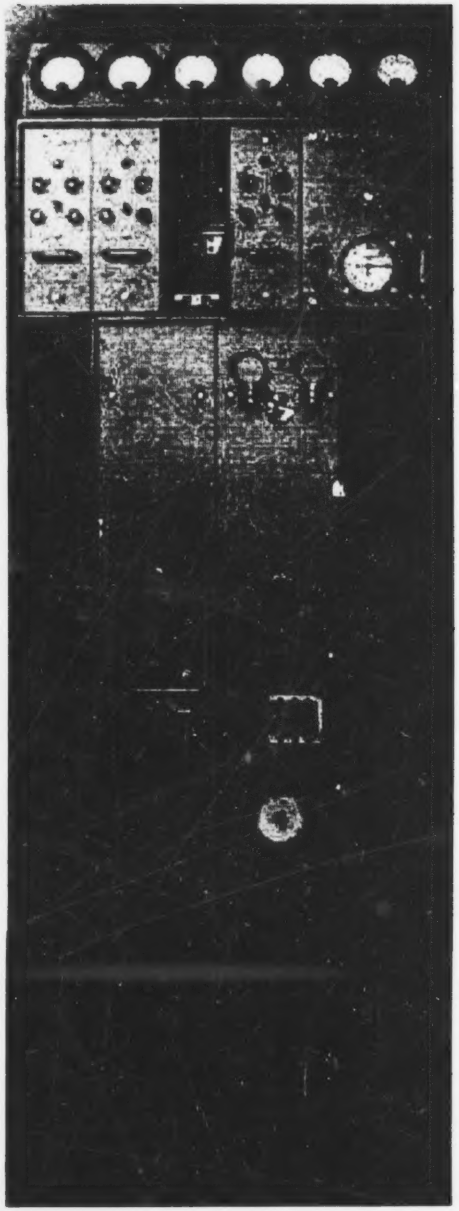
Mark-III Analyzer



Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freons

Mark- IV Analyzer



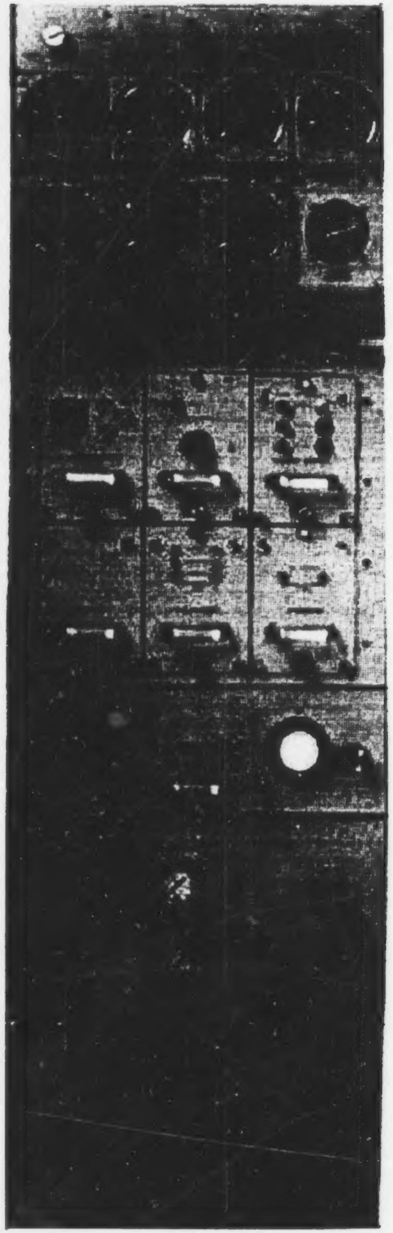
Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freon 12
- Freon 11

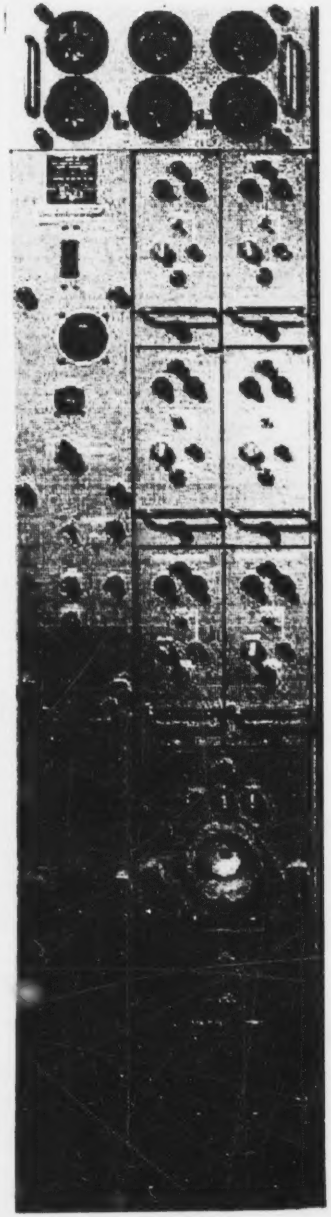
Mark- V Analyzer

Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freon 12
- Freon 114



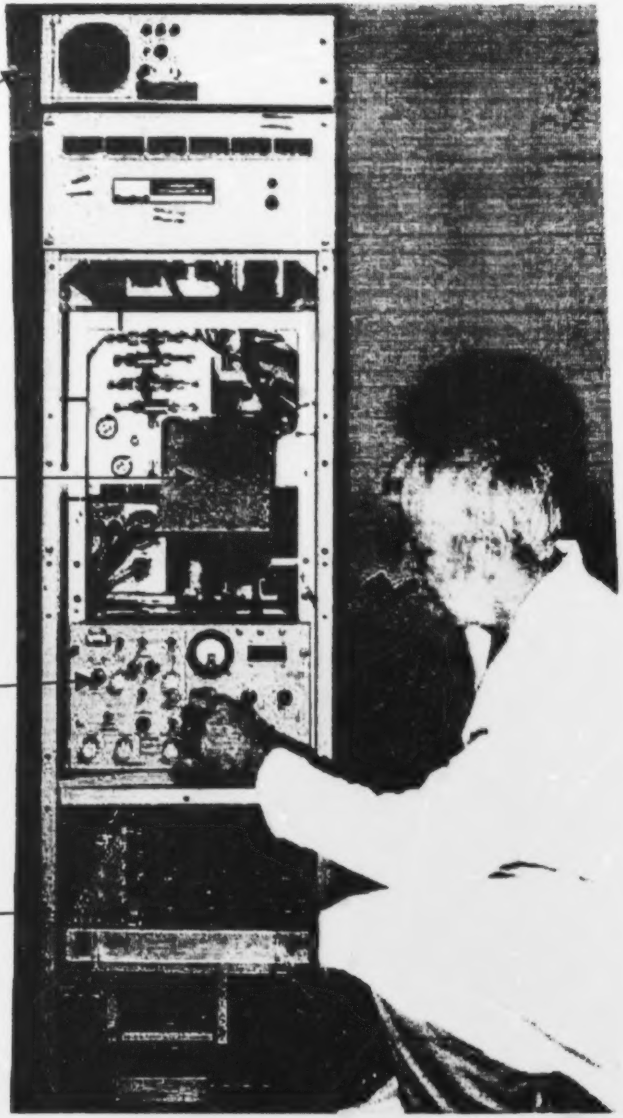
Mark- VI Analyzer



Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freon 12
- Freon 114

CAMS-I Prototype System
with the cover removed



Add-on carbon monoxide analyzer

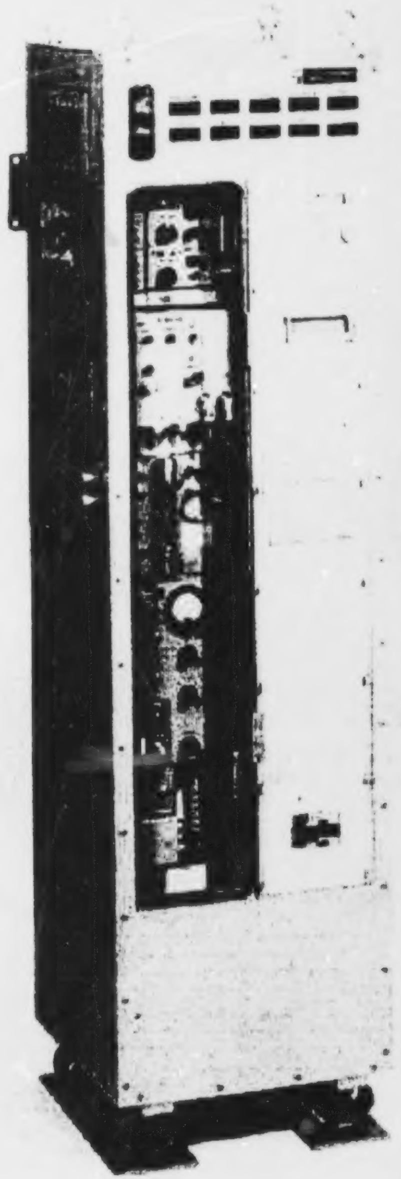
Mass Spectrometer

Control electronics

Power Supplies

CAMS-I

shown with the access
panel open



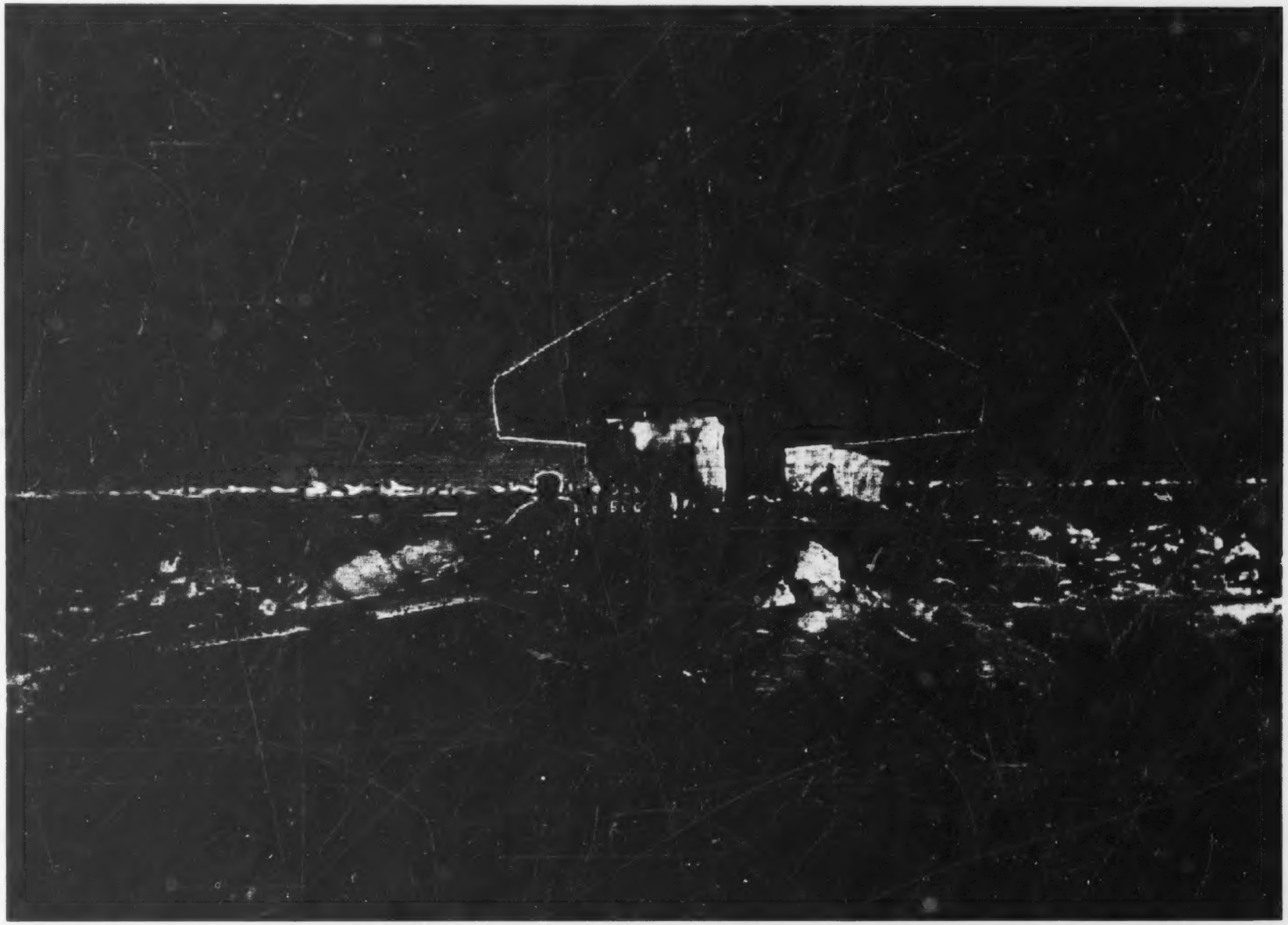
Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freon 12
- Freon 114

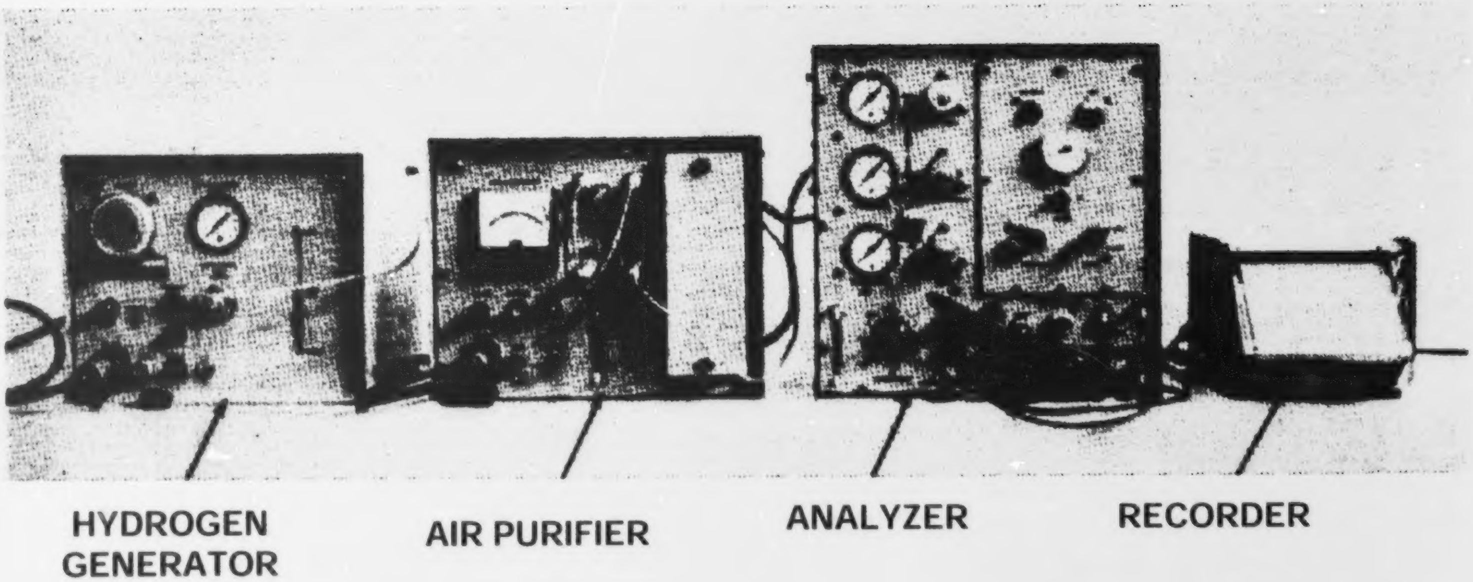
Dimensions

5 ft. high by 17 in. by 17 in.
(152x43x43 cm)

USS HAWKBILL at the North Pole in 1998

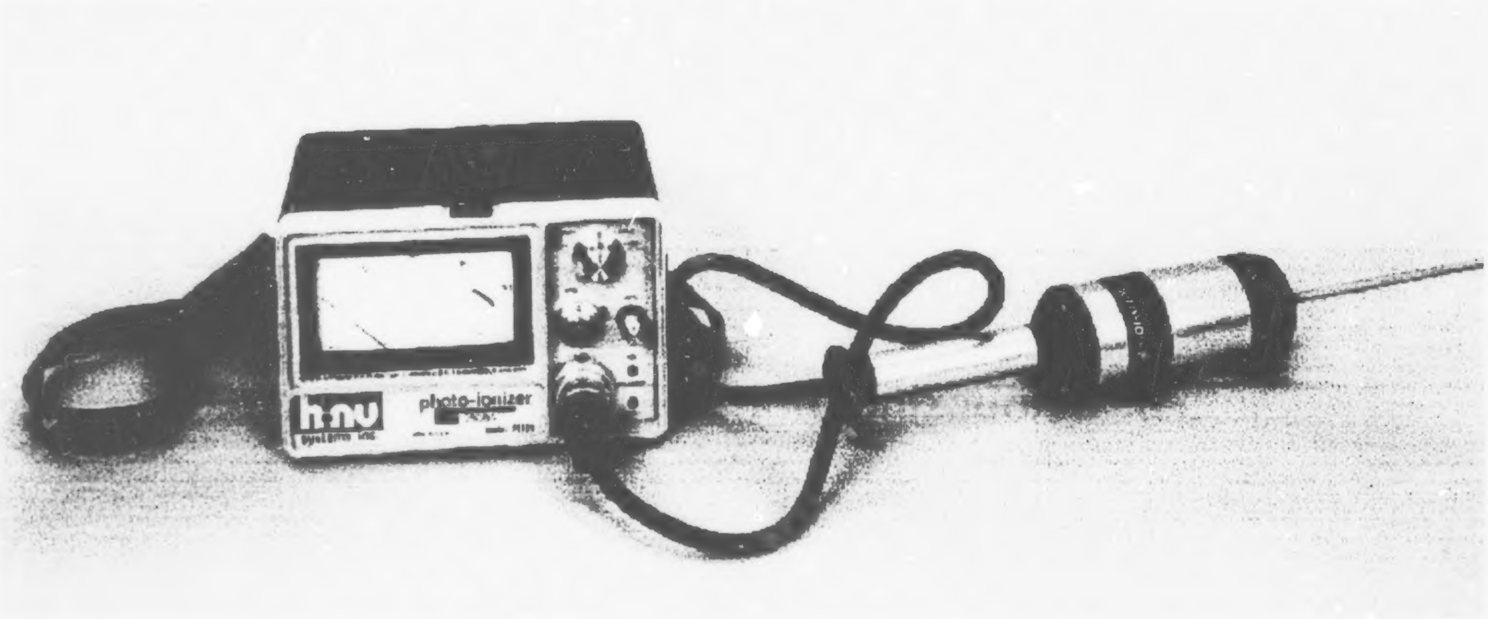


TRACE HYDROCARBON ANALYZER (THA)


HYDROGEN GENERATOR
AIR PURIFIER
ANALYZER
RECORDER

TRACE GAS ANALYZER (TGA)

Commercial Portable Photoionization Detector


hnu
systems inc
photo-ionizer

CAMS-I
PROGRAM CHRONOLOGY

Date	Event
1970	NASA system tested on the HAWKBILL
1971	Two protoypes designed and built
1972	Prototypes tested on the HAWKBILL and PINTADO
1973	Production contract awarded
1975	First production system Installed
1979	All old systems replaced with CAMS

CAMS-II
PROGRAM CHRONOLOGY

Date	Event
1975	Specifications Created
1978	Proposals Submitted
1979	Contract Awarded
1981	System Designed, Hardware built
1982	Factory Testing Completed
1983	Testing at NRL
1984	Initial installation on USS SUNFISH (4/84)
1984	Return to factory to correct drift problem (11/84)
1985	Reinstalled (1/85)

CAMS-II
PROGRAM CHRONOLOGY
(cont)

Date	Event
1985	Returned to factory to correct problems (4/85)
1985	Problems fixed, burn-in testing begun (8/85)
1986	Reinstalled TECHEVAL Begins (4/86)
1987	OPEVAL Begins (1/87), parallel factory testing
1988	OPEVAL Ends (1/88)
1989	Production Contract Begun, many electronics upgrades
1992	First Production Installation USS KENTUCKY
1993-2000	Software upgrades
2000	Installed on all Trident and Seawolf submarines

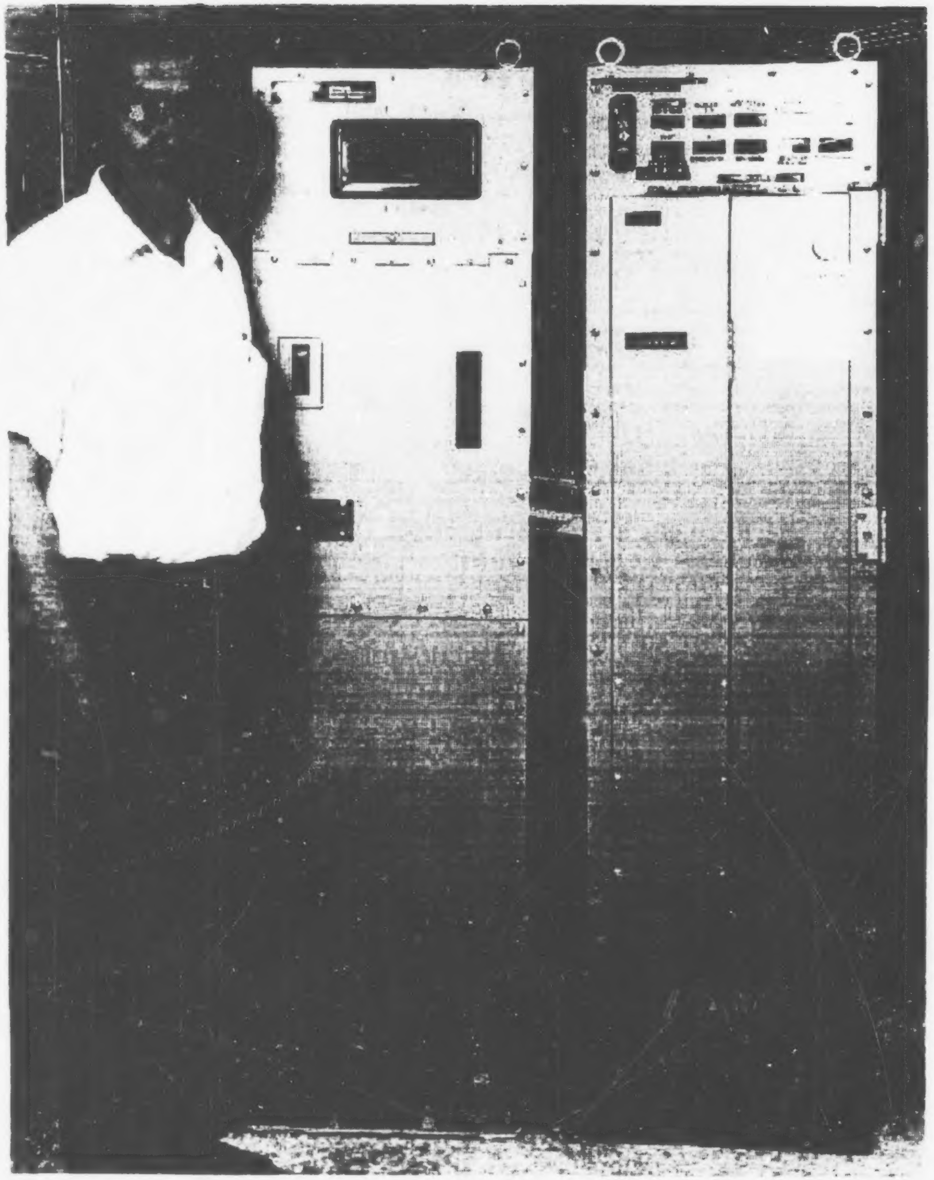
CAMS-II

shown left of CAMS-I
during NRL lab test

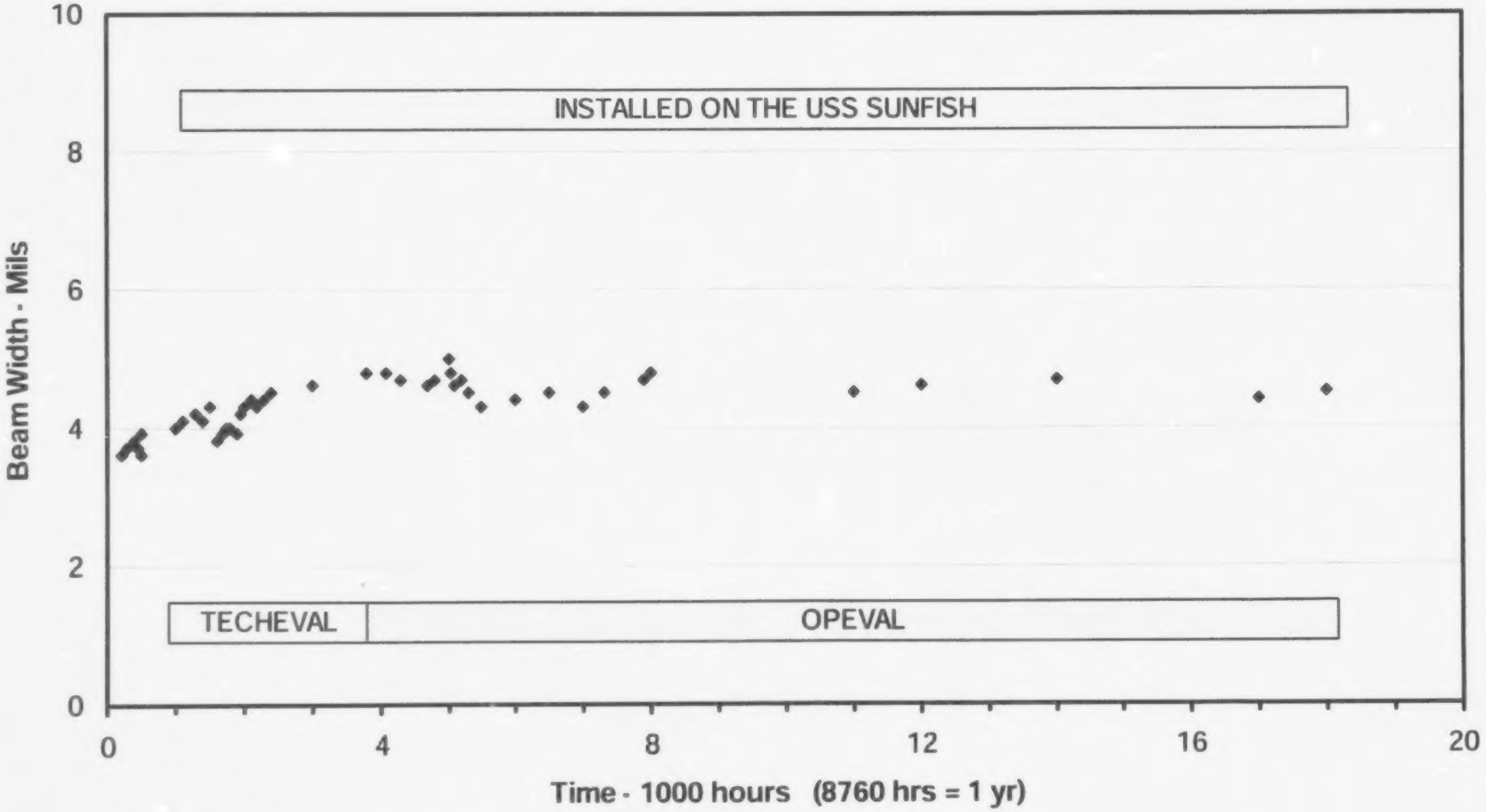
Gases Analyzed

- Hydrogen
- Oxygen
- Carbon Dioxide
- Carbon Monoxide
- Freon 12, 134a
- Freon 114
- Aliphatic Hydrocarbons
- Aromatic Hydrocarbons
- many more optional

Dimensions
Identical to CAMS-I



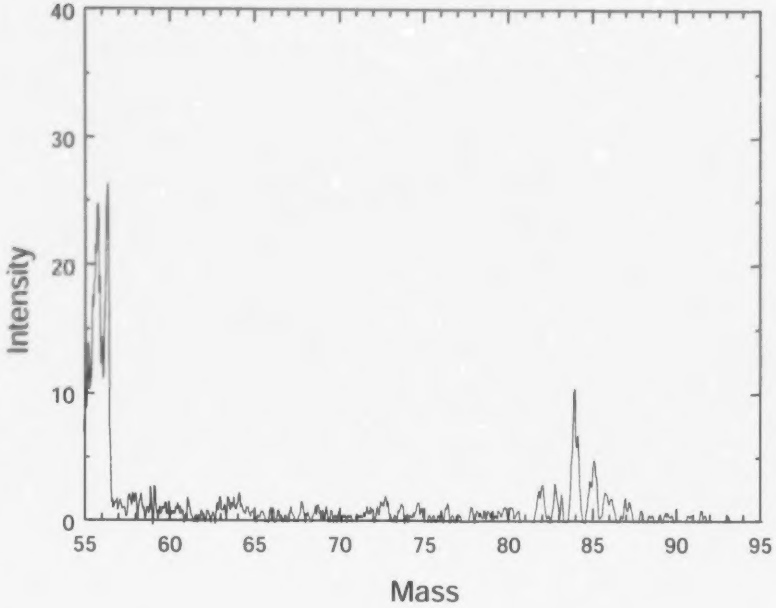
CAMS-II Shipboard Stability Test Results



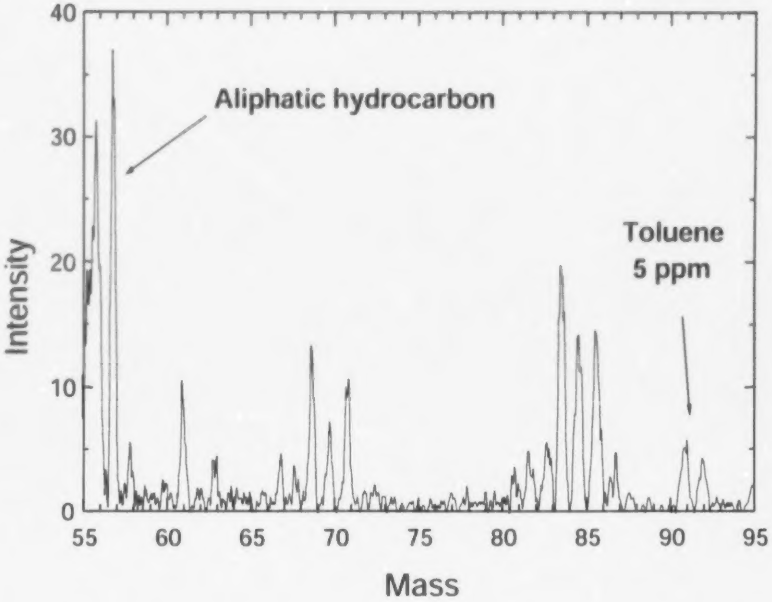
CAMS-II Data Taken In Port

Showing the detection of paint solvents
in the submarine atmosphere

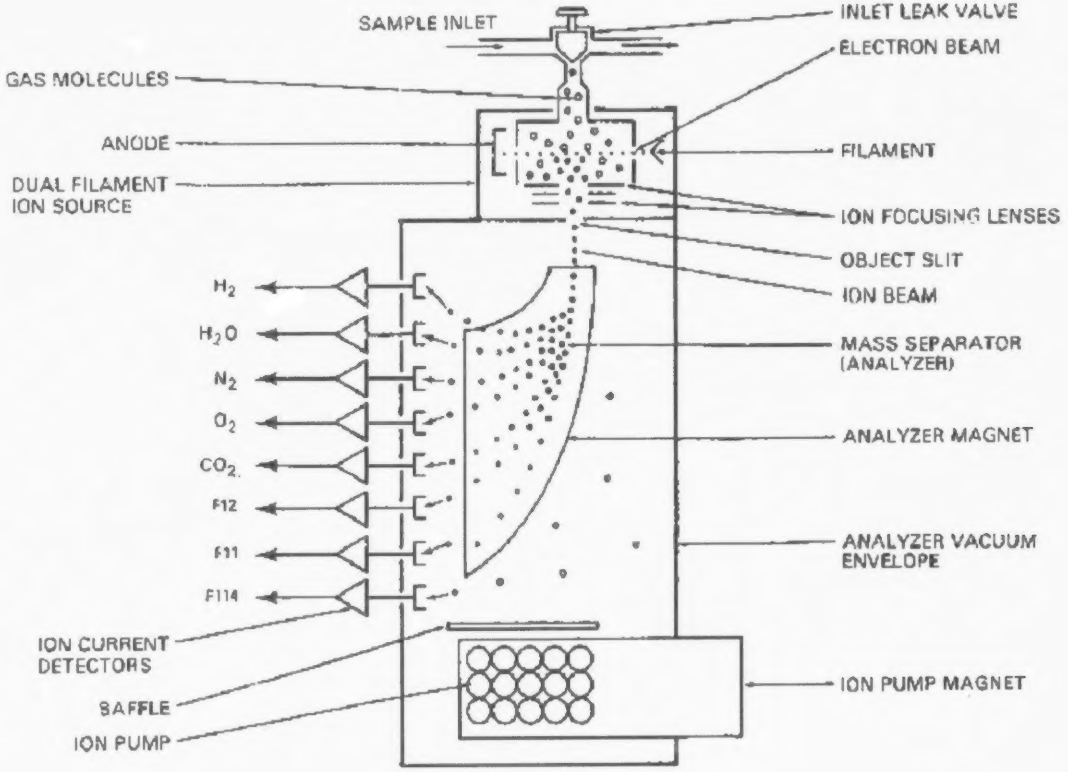
Single CAMS-II Spectrum
In Port (SSBN 737)



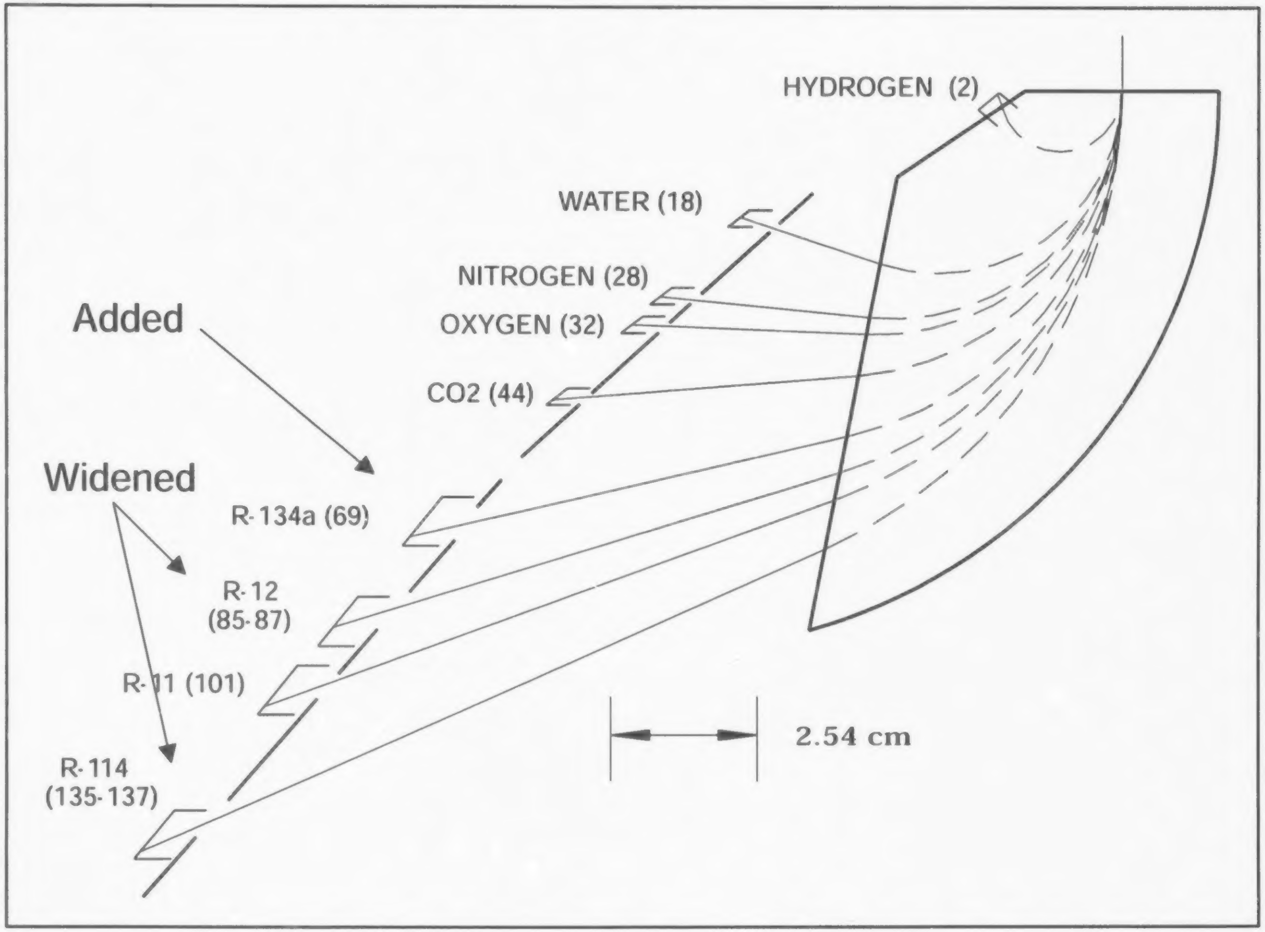
Single CAMS-II Spectrum
In Port while Painting (SSBN 737)



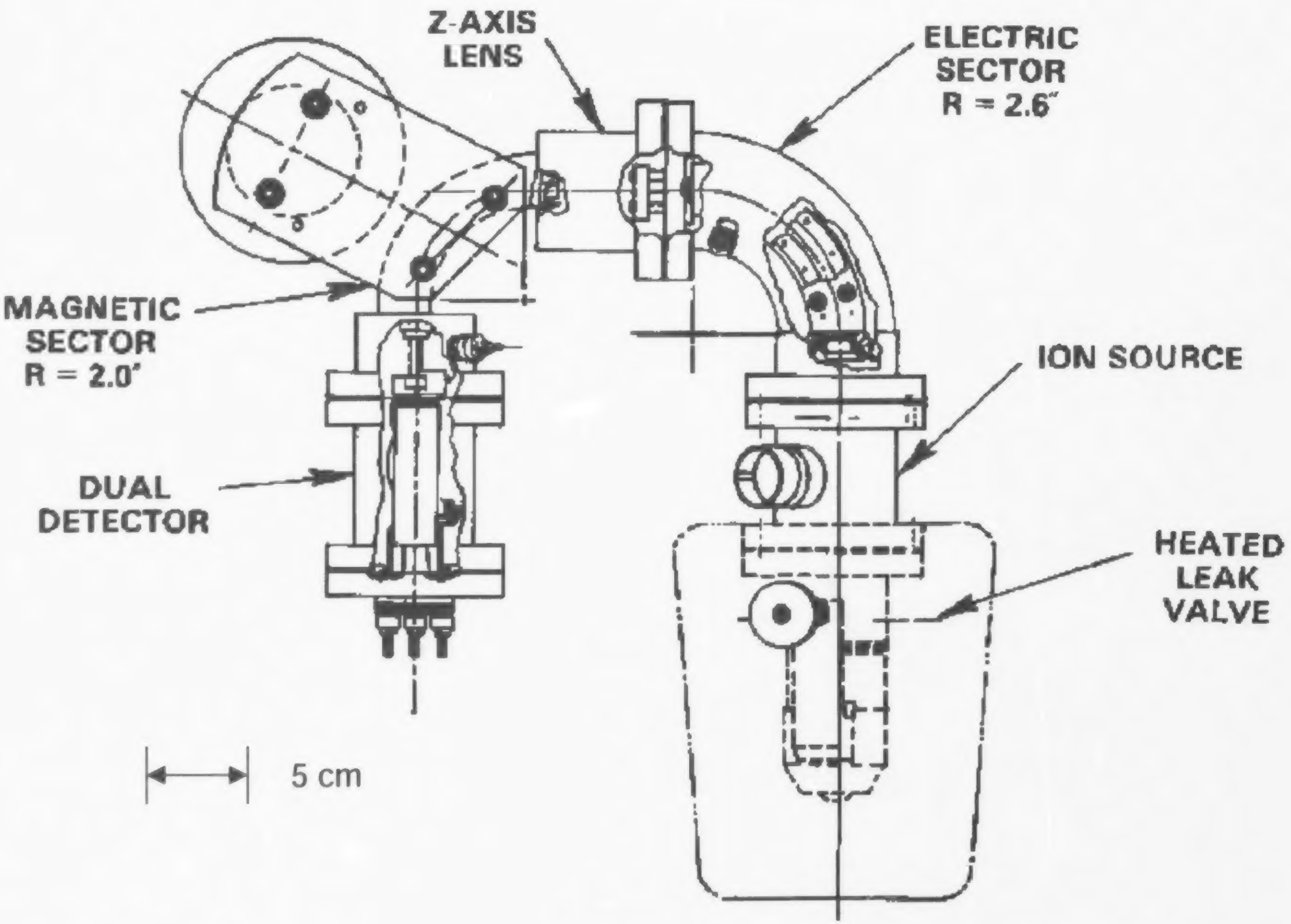
CAMS-I SCHEMATIC DRAWING


SAMPLE INLET
INLET LEAK VALVE
ELECTRON BEAM
GAS MOLECULES
ANODE
FILAMENT
DUAL FILAMENT ION SOURCE
ION FOCUSING LENSES
OBJECT SLIT
ION BEAM
H_2
H_2O
MASS SEPARATOR (ANALYZER)
N_2
O_2
ANALYZER MAGNET
CO_2
F12
F11
ANALYZER VACUUM ENVELOPE
F114
ION CURRENT DETECTORS
BAFFLE
ION PUMP MAGNET
ION PUMP

CAMS-I SHOWING HFC MODIFICATION


HYDROGEN (2)
WATER (18)
NITROGEN (28)
OXYGEN (32)
CO2 (44)
Added
Widened
R-134a (69)
R-12
(85-87)
R-11 (101)
R-114
(135-137)
2.54 cm

CAMS-II SCHEMATIC DRAWING



Z-AXIS
LENS
ELECTRIC
SECTOR
R = 2.6"
MAGNETIC
SECTOR
R = 2.0"
ION SOURCE
DUAL
DETECTOR
HEATED
LEAK
VALVE
5 cm

Air Analysis 1959

Sample Analysis from carbon sampler used on the USS SKATE in 1959, reported hydrocarbon concentration was 75 mg/M^3

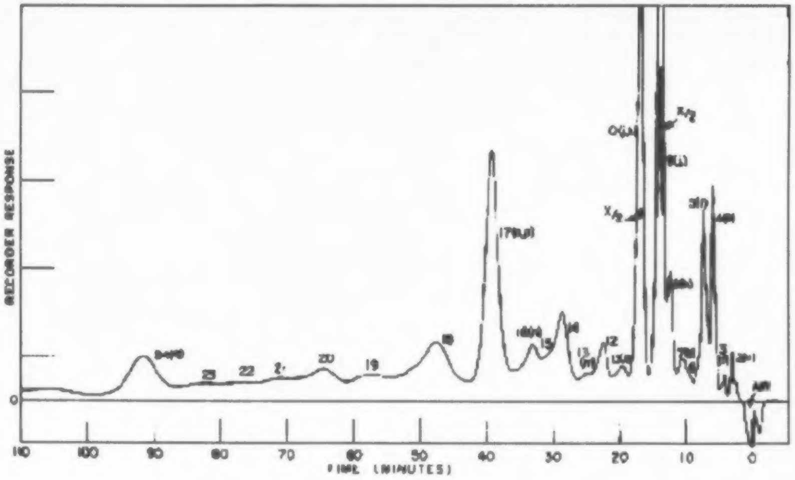


Figure 5 - Oil Desorbed from Canister No. 6. Squalane 75°C

comparison to paint thinner

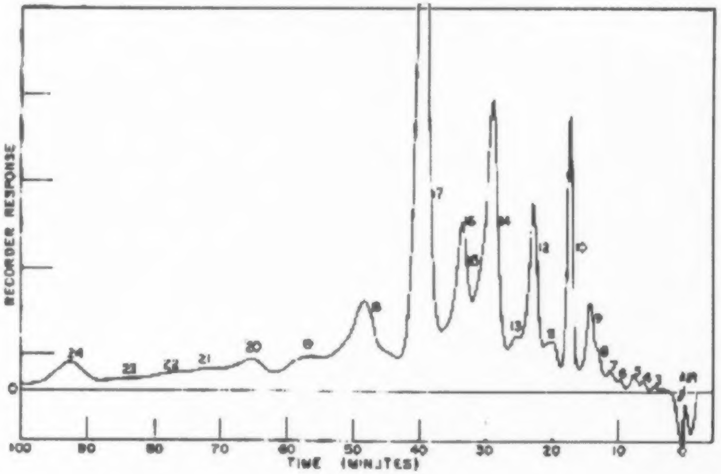
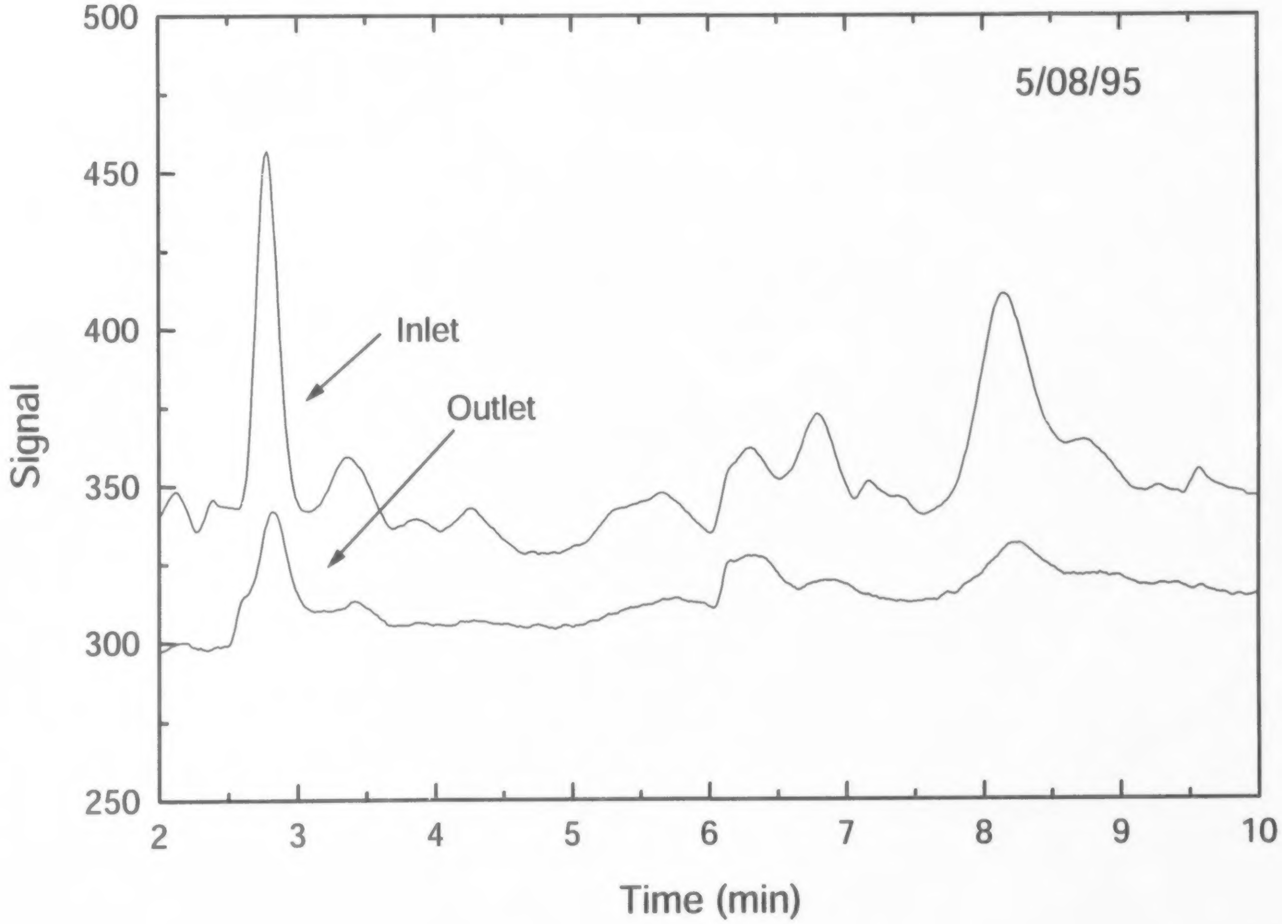


Figure 6 - Paint Thinner, Squalane 75°C

NRL Memo Report 1057, 1960

Data obtained using a portable gc showing the effect of the burner on submarine air



5/08/95

My Thoughts on Success of the CAMS Program

"Those who forget the past are doomed to repeat it" -- George Santayana (1900)

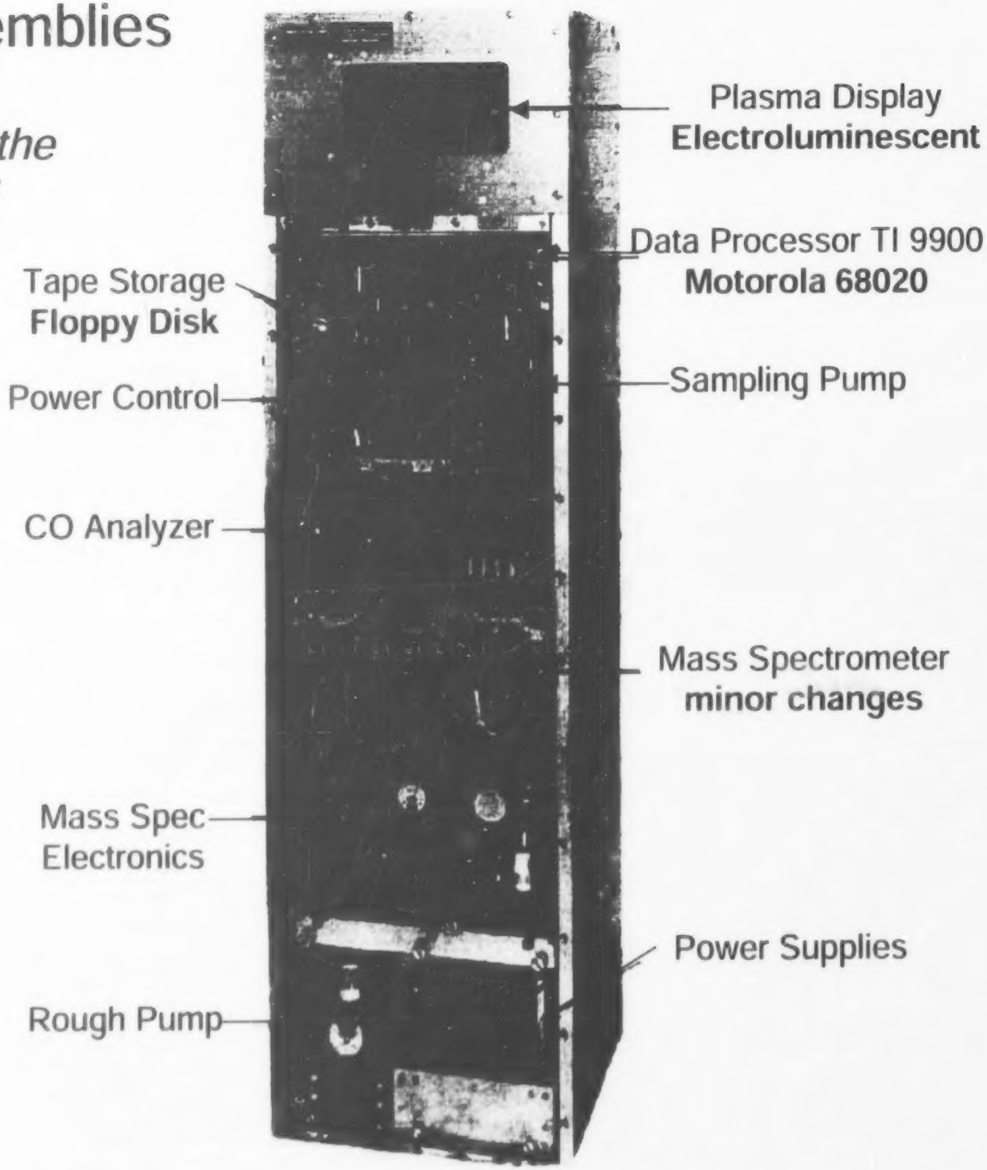
"Those who remember past successes can repeat them" -- Jeffrey Wyatt (2000)

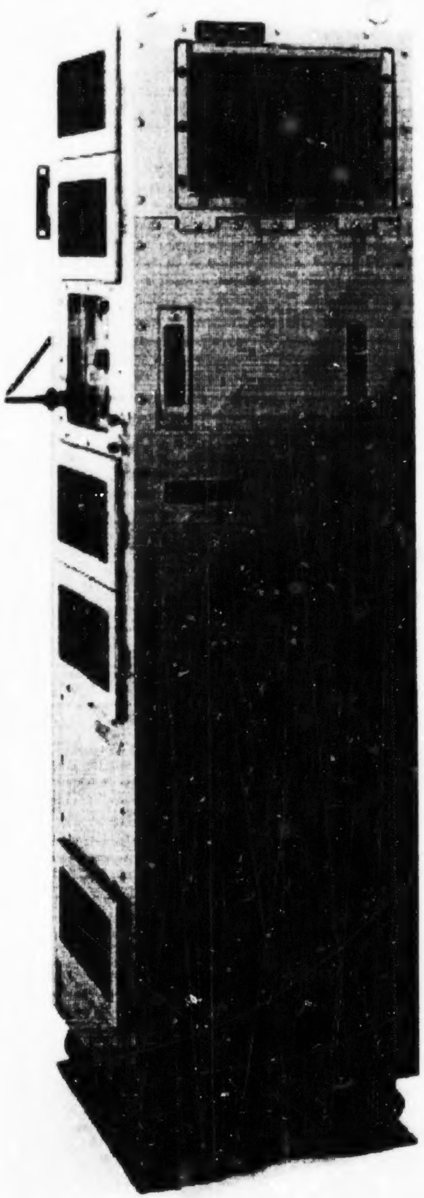
What I Remember

- Leadership with Vision
- Dedicated People
- Continuity in People
- Customer Participation
- Trust between the Navy and Vendor
- Get it right before starting production
- Time to Pause

CAMS-II Functional Assemblies

showing changes made to the production units in bold


Plasma Display
Electroluminescent
Data Processor TI 9900
Motorola 68020
Tape Storage
Floppy Disk
Sampling Pump
Power Control
CO Analyzer
Mass Spectrometer
minor changes
Mass Spec Electronics
Power Supplies
Rough Pump



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and Larry Stuart